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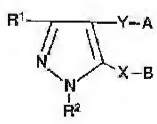
(54) **SUBSTITUTED PYRAZOLE DERIVATIVE AND GERMICIDE FOR AGRICULTURE AND HORTICULTURE**



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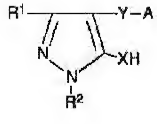

II

(57)Abstract:
PURPOSE: To provide a novel compound useful as a germicide for agriculture and horticulture.
CONSTITUTION: A compound of formula I [R1 is halogen, (halo)alkyl, alkoxy, alkylthio; R2 is (halo)alkyl; X is -N(R3)-, -CO-, -C(R4)(R5)-; Y is -O-,-S(O)-; (n) is 0-2; R3 is H, alkanoyl, etc.; R4, R5 are H, halogen, alkoxy, etc.; A is (substituted)phenyl; B is (substituted)heterocyclic group], e.g. 2-pyridyl-(4-(4- chlorophenylthio)-1,3-dimethyl-5-pyrazolyl)methanol. The compound of formula I is obtained by reacting a substituted pyrazole of formula II (X is -N(R3)-) with a heterocyclic compound of formula: L-B (L is a releasing group such as halogen), if necessary, in the presence of a base in a solvent. The compound of formula I is useful for plant diseases such as gray mold, rice sheath blight, melon downy mildew, and the melanose, powdery mildew, bitter rot and epidemic of citruses.

LEGAL STATUS

[Date of request for examination]

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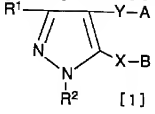
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1] Formula [1]: [Formula 1]



[1]

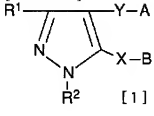
R1 expresses a halogen atom, an alkyl group, an alkoxy group, an alkylthio group, or a halo alkyl group among the [above-mentioned type. R2 An alkyl group or a halo alkyl group is expressed. X - N(R3)-, -CO-, or -C (R4) (R5) - It expresses. R3 A hydrogen atom, an alkyl group, a halo alkyl group, an alkenyl radical, an alkynyl group, and -COR6 -SO two R7 is expressed. Or R4 and R5 A hydrogen atom, a halogen atom, an alkyl group, a halo alkyl group, an alkenyl radical, an alkynyl group, or -OR8 is expressed independently, respectively. R8 A hydrogen atom, an alkyl group, a halo alkyl group, an alkenyl radical, an alkynyl group, An alkoxyalkyl group, a cyano alkyl group, an alkyl carbonyl alkyl group, The phenyl alkyl group and -COR6 which have an alkoxy carbonyl alkyl group, no permuting, or a substituent -SO two R7 is expressed. Or R6 The phenyl group which has a hydrogen atom, an alkyl group, a halo alkyl group, no permuting, or a substituent, The phenyl alkyl group, the alkoxy group, or -N (R9) which has no permuting or a substituent (R10) It expresses. R7 the phenyl group or -N (R9) (R10) which has an alkyl group, a halo alkyl group, no permuting, or a substituent expressing -- R9 and R10 The phenyl group which has a hydrogen atom, an alkyl group, no permuting, or a substituent independently, respectively is expressed. Y an oxygen atom, -S-, and -SO- or -- -SO2- is expressed, A expresses the phenyl group which has no permuting or a substituent, and B expresses the heterocycle radical which has no permuting or a substituent. However, for R1, X is -N (R3) at an alkyl group. - Except for the case of non-permuted 2-pyridyl radical, non-permuted 2-pyrimidyl radical, or non-permuted 2-pyrazyl radical in B.] The permutation pyrazol derivative come out of and expressed, or its salt.
[Claim 2] The permutation pyrazol derivative according to claim 1 which is the phenyl group in which A has more than a kind of the substituent chosen from the halogen atom, the alkyl group, and the halo alkyl group.
[Claim 3] X -N(R3)- it is -- permutation pyrazol derivative [claim 4] according to claim 2 Y -S- it is -- permutation pyrazol derivative according to claim 3.
[Claim 5] The permutation pyrazol derivative according to claim 4 whose R1 is a low-grade alkyl group or a halogen atom and whose R2 is a low-grade alkyl group.
[Claim 6] The permutation pyrazol derivative according to claim 5 which is the pyrimidyl

radical on which B has the pyridyl radical, no permuting, or the substituent which has no permuting or a substituent.
[Claim 7] The permutation pyrazol derivative according to claim 6 whose R1 is a halogen atom.
[Claim 8] The germicide for plantation arts which contains one sort of a permutation pyrazol derivative according to claim 1, or two sorts or more as an active principle.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the germicide for plantation arts which contains a new pyrazol derivative and this derivative as an active principle.
[0002]
[Description of the Prior Art] Although the germicide of former versatility has been developed, it cannot be said to be what it should not necessarily be satisfied with the effect, appearance of resistant bacteria, etc. of. Moreover, publication number 1-125379 It is indicated by a number official report, EP-459333A1, and JP,3-141276,A that a certain kind of pyrazol derivative has sterilization activity.
[0003]
[Problem(s) to be Solved by the Invention] Also in the compound indicated by the above-mentioned open official report, it should not be satisfied in respect of effect, residual effectiveness, phytotoxicity, etc., and development of the still more useful germicide for plantation arts is demanded to plant disease.
[0004]
[Means for Solving the Problem] As a result of repeating examination variously that this invention persons should develop the compound which has the outstanding sterilization activity in view of such a situation, the permutation pyrazol derivative shown by the following formula [1] resulted having the outstanding sterilization activity in header this invention. That is, this invention is formula [1]: [0005].
[Formula 2]



[1]

[0006] R1 expresses a halogen atom, an alkyl group, an alkoxy group, an alkylthio group, or a halo alkyl group among the [above-mentioned type. R2 An alkyl group or a halo alkyl group is expressed. X - N(R3)-, -CO-, or -C (R4) (R5) - It expresses. R3 A hydrogen atom, an alkyl group, a halo alkyl group, an alkenyl radical, an alkynyl group, and -COR6 -SO two R7 is expressed. Or R4 and R5 A hydrogen atom, a halogen atom,

an alkyl group, a halo alkyl group, an alkenyl radical, an alkynyl group, or -OR8 is expressed independently, respectively. R8 A hydrogen atom, an alkyl group, a halo alkyl group, an alkenyl radical, an alkynyl group, An alkoxyalkyl group, a cyano alkyl group, an alkyl carbonyl alkyl group, The phenyl alkyl group and -COR6 which have an alkoxy carbonyl alkyl group, no permuting, or a substituent -SO two R7 is expressed. Or R6 The phenyl group which has a hydrogen atom, an alkyl group, a halo alkyl group, no permuting, or a substituent, The phenyl alkyl group, the alkoxy group, or -N (R9) which has no permuting or a substituent (R10) It expresses. R7 the phenyl group or -N (R9) (R10) which has an alkyl group, a halo alkyl group, no permuting, or a substituent expressing -- R9 and R10 The phenyl group which has a hydrogen atom, an alkyl group, no permuting, or a substituent independently, respectively is expressed. Y an oxygen atom, -S-, and -SO- or -- -SO2- is expressed, A expresses the phenyl group which has no permuting or a substituent, and B expresses the heterocycle radical which has no permuting or a substituent. However, for R1, X is -N (R3) at an alkyl group. - Except for the case of non-permuted 2-pyridyl radical, non-permuted 2-pyrimidyl radical, or non-permuted 2-pyrazyl radical in B.] It is related with the germicide for plantation arts which comes out and contains the permutation pyrazol derivative expressed or its salt, and this derivative as an active principle.

[0007] In this invention, the substituent in the above-mentioned formula has following semantics. A halogen atom means a fluorine, chlorine, a bromine, and iodine, and shows a fluorine, chlorine, and a bromine preferably. The carbon number of the alkyl of an alkyl group, an alkoxy group, and an alkylthio group 1-6 are meant, respectively. For example, methyl, ethyl, n-, or i-propyl, n-, s-, i- or t-butyl, pentyl, hexyl, methoxy, Ethoxy **n- or i-propoxy, n-, s-, i- or t-butoxy, pentoxy, HEKISOKISHI, methylthio, ethyl thio, n- or i-propyl thio, n-, s-, i-, or t-butyl thio is mentioned. Preferably, methyl, ethyl, n- or i-propyl, n-, s-, i- or t-butyl, methoxy, and ethoxy **n- or i-propoxy, n-, s-, i-, or t-butoxy is mentioned.

[0008] The carbon number of the alkyl of a halo alkyl group means 1-6, for example, fluoro methyl, difluoromethyl, trifluoromethyl, chloromethyl, bromomethyl, trifluoroethyl, trichloroethyl, trifluoro propyl, etc. are mentioned. or [that the number of the substituents of the phenyl group which has a substituent is 1-5, and the class of the substituent is the same] -- or it may be different from each other. The phenyl group permuted as the substituent by a halogen atom, an alkyl group, a halo alkyl group, the alkoxy group, the alkylthio group, the nitro group, the cyano group, etc. is mentioned. however, n under above-mentioned definition -- normal -- in i, s expresses SEKANDARI and t expresses tertiary for ISO.

[0009] The heterocycle expressed with the above-mentioned B expresses the condensation heterocycle containing 5, 6 membered-ring heterocycle, or one or more nitrogen atoms containing one or more nitrogen atoms, for example, a pyridine, a pyrimidine, pyridazine, pyrazine, triazine, a pyrrole, a pyrazole, an imidazole, a thiazole, oxazole, etc. are mentioned. As the substituent, a halogen atom, an alkyl group, an alkoxy group, a halo alkyl group, a haloalkoxy radical, etc. are mentioned.

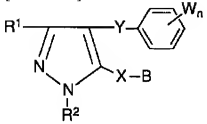
[0010] R1 As a substituent, it is a low-grade alkyl group or a halogen atom preferably, and a halogen atom is expressed more preferably. R2 As a substituent, an alkyl group is expressed preferably. -S- is expressed, X expresses -N(R3)- preferably, and Y is R3. A hydrogen atom or -CHO is expressed preferably. A expresses preferably the phenyl group

which has more than a kind of the substituent chosen from the halogen atom, the alkyl group, and the halo alkyl group, and B expresses preferably the pyrimidyl radical which has a halogen atom as the pyridyl radical which has a halogen atom as no permuting or a substituent, no permuting, or a substituent.

[0011] Next, this invention compound expressed with a formula [1] is shown in the 1st table. However, this invention compounds are not these things limited to seeing. Compound No. It is referred to in a next publication. In addition, Ph in each table About a phenyl group, it is i. About ISO, it is t. Et shows an ethyl group and Pr shows a propyl group for tertiary.

[0012] ** 1 Table [0013]

[Formula 3]



[0014] It comes out, it sets to the compound expressed, and is [0015].

[Table 1]

---------- Compound No. R1 R2 X Y Wn B ---------- 1 Cl CH3 NH S 4-Cl B1 2 Cl CH3 NH S 2 4-Cl2 B1 3 Cl CH3 NH S 3-Cl, 4-CH3 B1 4 Cl CH3NCHO S 4-Cl B1 5Cl(s) CH3 NH S 4-CH3 B1 6 Cl CH3NH S 2, 4-Cl2B1 7 Cl CH3 NHS2, 3-Cl2 B1 8 CH3O CH3 NH S 4-Cl B1 9 CH3O CH3 NH S 3-Cl, 4-CH3 B1 10 CH3O CH3 NH S 2, 4-Cl two B1 11CH(s)3O CH3 NH S 2-F, 4-CH3 B1 12 CH3O CH3 NH S 3-F, 4-CH3 B1 13 CH3OCH3 NCHO S 2 4-Cl2 B1 14 CH3O CH3 NCHO S 3-Cl, 4-CH3 B1 15 CH3S CH3 NH S 4-Cl B1 16 CH3S CH3 NH S 3 4-Cl2 B1 17CH(s)3S CH3 NH S 2 4-Cl2 B1 18 CH3S CH3 NH S 3-Cl, 4-CH3 B1 19 CH3S CH3 NH S 2-Cl, 4-CH3 B1 20CH(s)3S CH3 NH S 3-F, 4-CH three B121 Cl CH3 NH S 4-Cl B-2 22 ClCH3 NH S 2 4-Cl2 B-2 23 ClCH3 NCH3 S 4-Cl B1 ---------- [0016]

[Table 2]

** 1 Table (continuation) ---------- Compound No. R1 R2 X Y Wn B ---------- 24 Cl CH3 NCH3 S 2 4-Cl2 B1 25 Cl CH3 NCH3 S 3-Cl, 4-CH3 B1 26 Cl CH3 NEt S 4-Cl B1 27Cl(s) CH3 N-i-Pr S4-CH3 B1 28 Cl Et NH S 2 4-Cl2 B1 29 Cl i-PrNH S 2 4-Cl2 B1 30Cl(s) CHF2 NH S 4-Cl B1 31 Cl CHF2 NH S 3-Cl, 4-CH3 B1 32 Cl CF3 NHS 2, 4-Cl2 B1 33 Cl CF3 NHS 2-F, 4-CH3 B1 34 Cl CH3 NSO2CH3 S 3-F, 4-CH3 B1 35 Cl CH3 NSO2CH3 S 2 4-Cl2 B1 36 ClCH3 NSO2CH3 S 3-Cl, 4-CH3 B1 37Cl(s) CH3 NCH3S 3-Cl, 4-CH3 B-2 38Cl(s) CH3 NEt S 4-Cl B-2 39 Cl CH3 N-i-Pr S 4-CH3 B-2 40Cl Et NH S 2 4-Cl2 B241 Cl i-Pr NH S 2 4-Cl2 B-2 42 ClCHF2 NH S 4-Cl B-2 43 Cl CHF2 NH S 3-Cl, 4-CH3 B-2 44 Cl CF3 NHS 2 4-Cl2 B-2 45Cl CF3 NH S 2-F, 4-CH3 B-2 ---------- [0017]

[Table 3]

** 1 Table (continuation) ---------- Compound No. R1 R2 X Y Wn B ---------- 46 Cl CH3 NSO2CH3 S 3-F, 4-CH3 B-2 47 Cl CH3 NH S 4-Cl B3 48 Cl CH3 NH S 2 4-Cl2 B3 49Cl(s) CH3 NHS 3-Cl, 4-CH3 B4 50 Cl CH3 NH S 4-Cl B4 51 Cl CH3 NH S 4-CH3 B5 52Cl CH3 NH S 2 4-Cl2 B5 53 Cl CH3NHS 2 4-Cl2 B6

54 Cl CH3 NH S 4-Cl B6 55 Cl CH3 NH S 3-Cl, 4-CH3 B7 56 Cl CH3 NH S 2 4-Cl2 B7 57 Cl CH3 NH S 2-F, 4-CH3 B8 58 Cl CH3 NH S 3-F, 4-CH3 B9 59 Cl CH3 NH S 2 4-Cl2 B10 60 Cl CH3 NH S 3-Cl, 4-CH three B11 61 Cl CH3 NH S 3-Cl, 4-CH3 B12 62 Cl CH3 NH S 4-Cl B13 63 Cl CH3 NH S 4-CH3 B14 64 Cl CH3 NH S 2 4-Cl2 B15 65 Cl CH3 NH S 2 4-Cl2 B16 66 Cl CH3NH S 4-Cl B16 67 ClCH3 NH S 3-Cl, 4-CH3 B17 ---------- [0018]

[Table 4]

** 1 Table (continuation) ---------- Compound No. R1 R2 X Y Wn B ---------- 68 Cl CH3 NH S 2 4-Cl2 B17 69 Cl CH3 NH S 2-F, 4-CH3 B18 70 Cl CH3 NH S 3-F, 4-CH3 B18 71 CH3 CH3 CH2 S4-Cl B1 72 CH3 CH3 CH2 S 2 4-Cl2 B1 73 CH3 CH3CH2 S 2-Cl, 4-CH3 B1 74 CH3CH3 CH2 S 2-F, 4-CH three B175 CH3 CH3 CH (OH) S 4-Cl B1 76 CH3 CH3 CH (OH) S 2 4-Cl2 B1 77 CH3 CH3 CH (OH) S 2-Cl, 4-CH3 B1 78 CH3 CH3 CH (OH) S 3-Cl, 4-CH3 B1 79 CH3 CH3 CH (OH) S 2-F, 4-CH3 B1 80 CH3 CH3 CH (OH) S 3-F, 4-CH3 B1 81 CH3 CH3 CH (OCH3) S 4-Cl B1 82 CH3 CH3 CH (OCH3) S 2 4-Cl2 B1 83 CH3 CH3 CH (OCOCH3) S 4-Cl B184 CH3 CH3 CH (OCOCH3) S 2 4-Cl2 B1 85CH3 CH3 CH (OCOCH3) S 2-Cl, 4-CH3 B1 86 CH3 CH3 CH (OCOCH3) S 2-F, 4-CH three B1 87 CH3 CH3 CH (F) S 4-Cl B1 88 CH3 CH3 CH (F) S 2 4-Cl2 B1 89 CH3 CH3 CH (Cl) S 4-Cl B1 ---------- ---------- [0019]

[Table 5]

** 1 Table (continuation) ---------- Compound No. R1 R2 X Y Wn B ---------- 90 CH3 CH3 CH (Cl) S 2 4-Cl2 B1 91 CH3 CH3 C=O S 4-Cl B1 92 CH3 CH3 C=O S 2 4-Cl2 B1 93 CH3 CH3 C=O S2-Cl, 4-CH3 B1 94CH(s)3 CH3 C=O S 2-F, 4-CH three B1 95 CH3 CH3 CH2 S 4-Cl B-2 96CH3 CH3 CH2 S2, 4-Cl2 B-2 97 CH3 CH3 CH2 S 2-Cl, 4-CH3 B-2 98 CH3CH3 CH2 S 2-F, 4-CH3 B-2 99 CH3 CH3 CH (OH) S 4-Cl B-2 100 CH3 CH3 CH (OH) S 2 4-Cl2 B-2 101 CH3 CH3 CH (OH) S 2-Cl, 4-CH3 B-2 102 CH3 CH3 CH (OH) S 3-Cl, 4-CH3 B-2 103 CH3 CH3 CH (OH) S 2-F, 4-CH3 B-2 104 CH3 CH3 CH (OH) S 3-F, 4-CH3 B-2 105 CH3 CH3 CH (OCH3) S 4-Cl B-2 106 CH3 CH3 CH (OCH3) S 2, 4-Cl2B2 107 CH3 CH3 CH (OCOCH3) S 4-Cl B-2 108 CH3 CH3 CH (OCOCH3) S 2 4-Cl2 B-2 109 CH3 CH3 CH (OCOCH3) S 2-Cl, 4-CH3 B-2 110 CH3 CH3 CH (OCOCH3) S2-F, 4-CH3 B-2 111 CH3 CH3 CH (F) S 4-Cl B-2 ---------- [0020]

[Table 6]

** 1 Table (continuation) ---------- Compound No. R1 R2 X Y Wn B ---------- 112 CH3 CH3 CH (F) S 2 4-Cl2 B2113 CH3 CH3 CH (Cl) S 4-Cl B2114 CH3 CH3 CH (Cl) S 2 4-Cl2 B2115 CH3 CH3 C=OS 4-Cl B2116 CH3 CH3 C=OS 2 4-Cl2 B2117 CH3 CH3 C=O S 2-Cl, 4-CH3 B2118 CH3 CH3 C=O S 2-F, 4-CH3 B2119 CH3 CH3 C (CH3) (OH) S 4-Cl B2120 CH3 CH3 C (CH3) (OH) S 2 4-Cl2 B2121CH3 CH3 C (CH3) (OCOCH3) S 4-Cl B2122 CH3 CH3 C (CH3) (OCOCH3) S 2 4-Cl2 B2123 CH3 CH3 C (CH3) (F) S 4-Cl B2124 CH3 CH3 C (CH3) (F) S 2 4-Cl2 B2125CH3 CH3 C (Et), (OH) S 4-Cl B2126 CH3 CH3 C (Et) and (OH) S 2 4-Cl2 B2127 CH3 CH3 C (i-Pr) (OH) S 4-Cl B2128 CH3 CH3 C (i-Pr) (OH) S2 and 4-Cl2 B2129 CH3 CH3 C (i-Pr) (OH) S 2-Cl, 4-CH3 B2130 CH3 CH3 C (i-Pr) (OH) S 2-F and 4-CH3 B2131 CH3 CH3 CH (CH3) S 4-Cl B2132CH3 CH3 CH (CH3) S 2 4-Cl2 B2133CH3 CH3 CH (CH3) S 2-Cl, 4-CH3 B-2 ---------- [0021]

[Table 7]

** 1 Table (continuation) ---------- Compound No. R1 R2 X Y Wn B ---------- 134 CH3 CH3 CH (CH3) S 2-F, 4-CH3 B-2 135 Cl CH3 CH2 S 4-Cl B-2 136 Cl CH3 CH2 S 2 4-Cl2 B-2 137 Cl CH3 CH2 S 2-Cl, 4-CH3 B-2 138 Cl CH3 CH2 S 2-F, 4-CH3 B-2 139 CH3O CH3 CH2 S 4-Cl B-2 140 CH3O CH3 CH2 S 2, 4-Cl2 B-2 141 CH3O CH3 CH2 S 2-Cl, 4-CH3 B-2 142CH3O CH3 CH2 S 2-F, 4-CH3 B-2 143 CH3 CH3 NH S 4-Cl B19 144 CH3 CH3 NH S2-Cl B19 145 CH3 CH3 NH S 2 4-Cl2 B19 146 CH3 CH3 NH S 3-Cl, 4-CH3 B19 147 CH3 CH3 NH S 2-Cl, 4-CH3 B19 148 CH3 CH3 NH O 4-Cl B20 149CH3 CH3 NH S 2-Cl B20 150 CH3 CH3 NH S 2, 4-Cl2B20 151 CH3 CH3 NH S 3-Cl, 4-CH3 B20 152 CH3 CH3 NH S2-Cl, 4-CH3 B20 153 CH3 CH3 NCHO S 4-Cl B19 154 CH3 CH3 NCHO S 2-Cl B19 155 CH3 CH3NCHO S 2 4-Cl2 B19 ---------- [0022]

[Table 8]

** 1 Table (continuation) ---------- Compound No. R1 R2 X Y Wn B ---------- 156 CH3 CH3 NCHO S 3-Cl, 4-CH3 B19 157 CH3 CH3 NCHO S 2-Cl, 4-CH3 B19 158 CH3 C2H5 NH S 4-Cl B19 159 CH3 C2H5 NH S 2-Cl B19 160 CH3 C2H5 NH S 2 4-Cl2 B19 161CH3 C2H5 NH S 3-Cl, 4-CH3 B19 162 CH3 C2H5 NH S 2-Cl, 4-CH3 B19 163 CH3 C2H5 NH S 2-F, 4-CH3 B19 164 CH3 C2H5 NH S 3-F, 4-CH three B19 165 CF3 CH3 NH S 2 4-Cl2 B19 166 CF3 CH3 NH S 2, 4-Cl2B20 167 Cl CH3 NH S 3 4-Cl2 B1 168 Cl CH3 NH S 3-F, 4-CH3 B1 169 Cl CH3 NH S 3-Cl, 4-F B1 170 Cl CH3 NH S 3-F, 4-OCH3 B1 171 Cl CH3NH S 3-Cl, 4-OCH three B1 172 ClCH3 NH S 2-Cl, 4-CH3 B1 173 Cl CH3NH S 2-F, 4-Br B1 174 Cl CH3 NH S 2-F, 4-Cl B1175 Cl CH3 NH S 2-F, 4-CH3 B1 176 Cl CH3 NH S 2, 3, 4-Cl3 B1 177 Cl CH3 NH S 4-CH3 B-2 ---------- ---------- [0023]

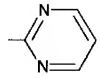
[Table 9]

** 1 Table (continuation) ---------- Compound No. R1 R2 X Y Wn B ---------- 178 Cl CH3 NH S 3 4-Cl2 B-2 179 Cl CH3 NH S 2-Cl-4-CH3 B-2 180 Cl CH3 NH S 3-Cl-4-CH3 B-2 181 ClCH3 NH S 2-F, 4-Cl B-2 182 ClCH3 NH S 2-F, 4-CH3 B-2 183 Cl CH3NH S 3-F, 4-CH3 B-2 184 Cl CH3 NHS 3-CH3, 4-CH3 B-2 185 Cl CH3 NH S2-F, 5-CH3 B-2 186 Cl CH3 NH S 3-Cl-4-F B-2 187 Cl CH3 NCHO S 4-CH3 B1 188 Cl CH3 NCHO S 3 4-Cl2 B1 189 Cl CH3 NCHO S 3-F, 4-CH3 B1 190 Cl CH3 NCHO S 2, 3, 4-Cl3 B1 191 Cl CH3 NCHO S 3-F, 4-CH3 B-2 192 Cl CH3 NH S 2-Cl B19 193 Cl CH3 NH S4-Cl B19 194 Cl CH3NH SO 4-CH three B19 195 Cl CH3NH SO2 4-CF3 B19 196 Cl CH3NH S 4-OCH3 B19 197 Cl CH3 NH S 2 4-Cl2 B19 198 Cl CH3 NH S 2-Cl, 4-CH3 B19 199 Cl CH3 NH S 3-Cl, 4-CH3 B19 ---------- ---------- [0024]

[Table 10]

** 1 Table (continuation) ---------- Compound No. R1 R2 X Y Wn B ---------- 200 Cl CH3 NH S 2-F, 4-Cl B19 201 Cl CH3 NH S 2-F, 4-CH3 B19 202 Cl CH3 NH S 2, 3, 4-Cl3 B19 203 Cl CH3 NCHO S H B19 204 ClCH3 NCHO S 2-Cl B19205 Cl CH3NCHO S 4-Cl B19 206 Cl CH3 NCHO S 4-CH3 B19 207 Cl CH3NCHO S 4-CF3 B19 208 Cl CH3 NCHO S 4-OCH3 B19 209 Cl CH3 NCHO S 2 4-Cl2 B19 210 Cl CH3 NCHOS 2-Cl, 4-CH3 B19 211 Cl CH3 NCHO S 3-Cl, 4-CH3 B19212 Cl CH3 NCHO S 2-F, 4-Cl B19 213 Cl CH3 NCHO S 2-F, 4-CH3 B19 214 ClCH3 NCHO S 2, 3, 4-Cl3 B19 215 Cl CH3 NH S H B20 216 Cl CH3 NH S 2-Cl B20 217 Cl CH3 NH S 4-Cl B20 218 Cl CH3 NH S 4-CH3 B20 219 Cl CH3 NH S 4-CF3 B20 220 Cl CH3 NH S 4-OCH3 B20 221 Cl CH3 NH S2, 4-Cl2 B20 ----------

----- [0025]
[Table 11]
** 1 Table (continuation) ---------- Compound No. R1 R2 X Y Wn B ---------- 222 Cl CH3 NH S 2-Cl, 4-CH3 B20 223 Cl CH3 NH S 3-Cl, 4-CH3 B20 224 Cl CH3 NH S 2-F, 4-Cl B20 225 Cl CH3 NH S 2-F, 4-CH3 B20 226 Cl CH3 NH S 2, 3, 4-Cl three B20 227 Cl CH3 NCHO S H B20 228 Cl CH3NCHO S 2-Cl B20 229 Cl CH3 NCHO S4-Cl B20 230 Cl CH3 NCHO S 4-CH three B20 231 Cl CH3 NCHO S 4-CF3 B20 232 Cl CH3 NCHO S 4-OCH three B20 233 ClCH3 NCHO S 2 4-Cl2 B20 234 Cl CH3 NCHO S 2-Cl, 4-CH3 B20 235 Cl CH3 NCHO S 3-Cl, 4-CH3 B20 236 Cl CH3NCHO S 2-F, 4-Cl B20 237 Cl CH3 NCHO S 2-F, 4-CH3 B20 238 Cl CH3 NCHO S 2, 3, 4-Cl3 B20 239 Br CH3 NH S H B19 240 Br CH3 NH S 2-Cl B19 241 Br CH3 NH S 2 4-Cl2 B19 242 Br CH3 NH S 3-Cl, 4-CH3 B19 243 Br CH3 NH S 3-F, 4-CH3 B19 ---------- [0026]
[Table 12]
** 1 Table (continuation) ---------- Compound No. R1 R2 X Y Wn B ---------- 244 Br CH3 NH S 2, 3, 4-Cl3 B19 245 Br CH3 NCHO S 4-Cl B19 246 Br CH3 NCHO S 2 4-Cl2 B19 247 Br CH3 NH S 2 4-Cl2 B20 248 Br CH3 NH S 3-Cl, 4-CH3 B20 249Br CH3 NH S 3-Cl, 4-CH3 B21 250 Br CH3NH S 3-F, 4-CH three B21 251Br CH3 NH S4-Cl B22 252 Br CH3 NH S 2 4-Cl2 B22 253 Br CH3 NH S 2 4-Cl two B23 254 Br CH3 NH S 3-F, 4-CH3 B23 255 Br CH3 NH S 2 4-Cl2 B24 256 Br CH3 NH S 3-Cl, 4-CH3 B24 257 Br CH3 NH S 3-F, 4-CH3 B25 258 Br CH3 NH S 2, 3, 4-Cl3 B25 259 Br CH3 NH S 2 4-Cl2 B26 260 F CH3 NH S 2, 4-Cl2B19 261 F CH3NH S 3-Cl, 4-CH3 B20 262 F CH3 NH S 3-Cl, 4-CH3 B21 263 CH3 CH3 NH S 2 4-Cl2 B21264 CH3 CH3 NH S 3-Cl, 4-CH3 B21265 CH3 CH3 NH S 3-F, 4-CH3 B21 ---------- [0027]
[Table 13]
** 1 Table (continuation) ---------- Compound No. R1 R2 X Y Wn B ---------- 266 CH3 CH3 NH S 2-F, 4-CH3 B21267 CH3 CH3 NH S 2-Cl, 4-CH3 B21268 Cl CH3 NH S 2 4-Cl two B21269 Cl CH3 NH S 3-Cl, 4-CH three B21270 CH3 CH3 NH S4-Cl B22271 CH3 CH3 NH S 2 and 4-Cl2 B22272 CH3 CH3 NH S 3-Cl, 4-CH3 B22273Cl CH3 NH S 2 4-Cl2 B22274 Cl CH3 NH S 3-Cl, 4-CH3 B22275 CH3 CH3 NH S 2 4-Cl2 B23276 CH3 CH3 NH S 3-Cl, 4-CH3 B23277 CH3 CH3 NH S 2-F, 4-Cl B23278 CH3 CH3 NH S 3-F, 4-CH3 B23279 Cl CH3 NH S 3-Cl, 4-CH3 B23280 CH3 CH3 NH S 2 4-Cl2 B24281 CH3 CH3 NH S 3-Cl, 4-CH3 B24282 Cl CH3 NH S 2 4-Cl2 B24283 Cl CH3 NH S 3-Cl, 4-CH3 B24284CH3 CH3 NH S 2, 4-Cl2B25285 Cl CH3 NH S 3-Cl, 4-CH3 B25286 CH3 CH3 NH S B1-B26 express the following chemical structures all over the 2 and 4-Cl2 B26 ---------- ---------- above-mentioned table.
[0028]
[Formula 4]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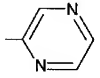
B2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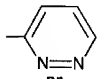
B4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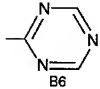
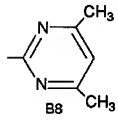

B6

[0029]
[Formula 5]


B7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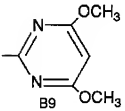
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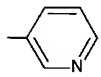
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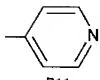
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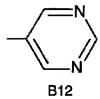
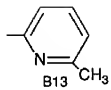

B12

[0030]
[Formula 6]



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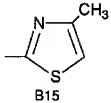

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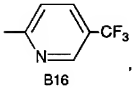

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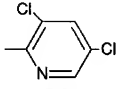

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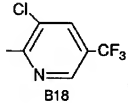

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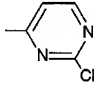

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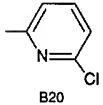
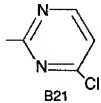


B20 ,

[0031]
[Formula 7]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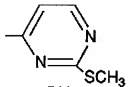
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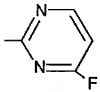
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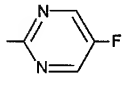
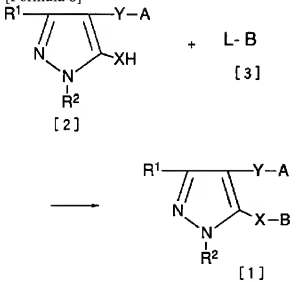

B26

[0032] Next, a reaction scheme shows the manufacturing method of this invention compound, and it explains below.

[0033] Reaction scheme (process 1)

[0034]

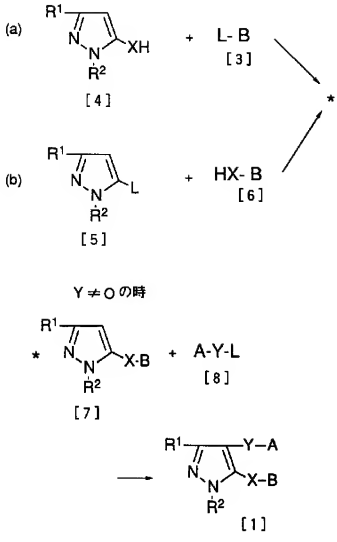
[Formula 8]



[0035] (Process 2)

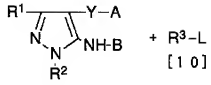
[0036]

[Formula 9]

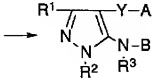


[0037] (Process 3)
[0038]
[Formula 10]

X=N-R³, R³ ≠ H の時

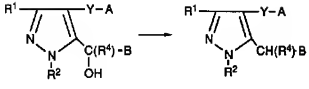


[9] [10]



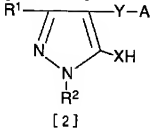
[11]

[0039] (Process 4)
[0040]
[Formula 11]
X=CH(R⁴)の時



[12] [13]

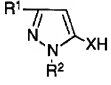
[0041] (Process 1)
Formula [2]: [0042]
[Formula 12]



[2]

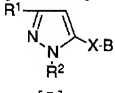
[0043] R1, R2, Y, and A express the same semantics as the above among [type, and X expresses -N(R3)-.] The permutation pyrazole come out of and shown, and formula [3]:L-B [3]
L expresses leaving groups, such as a halogen atom, among [type, and B expresses the same semantics as the above.] this invention compound can be manufactured by coming

out and making the heterocycle shown react. in this case, X of a formula [2] -NCOR4 or -NSO two R5 it is -- the time -- after treatment etc. -- setting -- hydrolysis -- receiving -- X of a product It may be obtained by -NH.
[0044] In the above-mentioned reaction, although a solvent is not necessarily required, as a solvent used, polar solvents, such as nitril, such as ester, such as ether, such as halogenated hydrocarbon, such as hydrocarbons, such as toluene, a xylene, and chlorobenzene, and a dichloroethane, diisopropyl ether, and dioxane, and ethyl acetate, and an acetonitrile, dimethyl sulfoxide, and dimethylformamide, are mentioned, for example. Moreover, organic bases (a pyridine, triethylamine, etc.) and inorganic bases (potassium carbonate, sodium hydride, etc.) may be added if needed.
[0045] Moreover, copper salt and a copper complex may be added as a catalyst if needed. The range of the heterocycle shown by the formula [3] to 1Eq of permutation pyrazoles the amount of the agent used for the above-mentioned reaction is indicated to be by the formula [2] is 1-5Eq. Although reaction temperature is obtained for arbitration in the above-mentioned reaction, room temperature -200 degree C or the reflux temperature of a solvent is usually desirable. After reaction termination can obtain the specified substance by performing the usual after treatment.
[0046] (Process 2)
(a) Formula [4]: [0047]
[Formula 13]



[4]

[0048] R1 and R2 express the same semantics as the above among [type, and X expresses -N(R3)-.] It is formula [7]: [0049] by making the heterocycle which comes out and is shown by the pyrazole shown and the formula [3] react using a suitable solvent and a suitable base if needed.
[Formula 14]



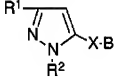
[7]

[0050] R1, R2, X, and B express the same semantics as the above among [type.] It manufactures. in this case, X of a formula [4] -NCOR4 or -NSO two R5 it is -- the time -- after treatment etc. -- setting -- hydrolysis -- receiving -- X of a formula [7] It may be obtained by -NH. In the above-mentioned reaction, polar solvents, such as nitril, such as ester, such as ether, such as halogenated hydrocarbon, such as hydrocarbons, such as toluene, a xylene, and chlorobenzene, and a dichloroethane, diisopropyl ether, and dioxane, and ethyl acetate, and an acetonitrile, dimethyl sulfoxide, and dimethylformamide, are mentioned as a solvent used, for example.

[0051] Moreover, as a base used, potassium carbonate, sodium hydride, etc. are mentioned, for example. Moreover, copper salt, a copper complex, etc. may be added as a catalyst if needed. Although reaction temperature is obtained for arbitration in the above-mentioned reaction, room temperature -200 degree C or the reflux temperature of a solvent is usually desirable.
[0052] (b) Formula [5]: [0053]
[Formula 15]

[5]

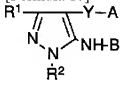
[0054] R1 and R2 express the same semantics as the above among [type, and L expresses leaving groups, such as a halogen atom.] The pyrazole come out of and shown, and formula [6]:HX-B [6]
B expresses the same semantics as the above among [type, and X expresses -N(R3)-.] It is formula [7]: [0055] by coming out and making the heterocycle shown react using a suitable solvent and a suitable base if needed.
[Formula 16]



[7]

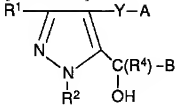
[0056] R1, R2, X, and B express the same semantics as the above among [type.] It manufactures. in this case, X of a formula [6] -NCOR4 or -NSO two R5 it is -- the time -- after treatment etc. -- setting -- hydrolysis -- receiving -- X of a formula [7] -NH It may be obtained. In the above-mentioned reaction, polar solvents, such as nitril, such as ester and an acetonitrile, dimethyl sulfoxide, and dimethylformamide, are mentioned to ether, such as halogenated hydrocarbon, such as hydrocarbons, such as toluene, a xylene, and chlorobenzene, and a dichloroethane, diisopropyl ether, and dioxane, ethyl acetate, etc. as a solvent used, for example.
[0057] Moreover, potassium carbonate, sodium hydride, etc. are mentioned as a base used. Moreover, copper salt, a copper complex, etc. may be added as a catalyst if needed. Although reaction temperature is obtained for arbitration in the above-mentioned reaction, room temperature -200 degree C or the reflux temperature of a solvent is usually desirable.
[0058] The next above (a) Or (b) The pyrazole shown by the obtained formula [7], and formula [8]:A-Y-L [8]
As for the inside A of [type, the same semantics as the above is expressed, Y expresses the same semantics as the above except an oxygen atom, and L expresses leaving groups, such as a halogen atom.] this invention compound can be manufactured by coming out and making the compound shown react using a suitable solvent and a suitable base if

needed.
[0059] In the above-mentioned reaction, polar solvents, such as nitril, such as ester, such as ether, such as halogenated hydrocarbon, such as hydrocarbons, such as toluene, a xylene, and chlorobenzene, a dichloroethane, chloroform, and a carbon tetrachloride, diisopropyl ether, and dioxane, and ethyl acetate, and an acetonitrile, dimethyl sulfoxide, and dimethylformamide, are mentioned as a solvent used, for example.
[0060] Moreover, a pyridine, triethylamine, potassium carbonate, etc. are mentioned as a base used. Although reaction temperature is obtained for arbitration in the above-mentioned reaction, 0 degree C - 100 degrees C are usually desirable.
(Process 3) It is formula [9]: [0061] at the time of X=N-R3 and R3 !=H.
[Formula 17]



[9]

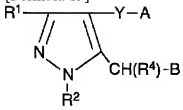
[0062] R1, R2, Y, A, and B express the same semantics as the above among [type.] Pyrazole come out of and shown, and formula [10]:R3-L [10]
R3 expresses the same semantics as the above except a hydrogen atom among [type, and L expresses leaving groups, such as a halogen atom.] this invention compound can be manufactured by coming out and making the compound shown react using a suitable solvent and a suitable base if needed.
[0063] In the above-mentioned reaction, polar solvents, such as nitril, such as ester, such as ether, such as halogen hydrocarbons, such as hydrocarbons, such as benzene, toluene, and a xylene, a dichloroethane, chloroform, and a carbon tetrachloride, diisopropyl ether, a tetrahydrofuran, and dioxane, and ethyl acetate, and an acetonitrile, dimethyl sulfoxide, and dimethylformamide, are mentioned as a solvent used, for example.
[0064] Moreover, as a base used, inorganic bases, such as organic bases, such as a pyridine and triethylamine, and potassium carbonate, sodium hydride, are mentioned. In the above-mentioned reaction, although reaction temperature is obtained for arbitration, 0 degree C - 100 degrees C are usually desirable.
[0065] (Process 4) It is formula [12]: [0066] at the time of X=CH (R4).
[Formula 18]



[12]

[0067] R1, R2, Y, A, B, and R4 express the same semantics as the above among [type.] By coming out and making the compound shown react using a suitable reducing agent, it is formula [13]: [0068].

[Formula 19]



[13]

[0069] R1, R2, Y, A, B, and R4 express the same semantics as the above among [type.] It can come out and this invention compound shown can be manufactured. as the reducing agent used in the above-mentioned reaction -- P2 I4 etc. -- the Lynn system compound is mentioned.

[0070]

[Example] Next, the concrete example of manufacture is shown.

[0071] [The example 1 of manufacture] (composition of this invention compound No.99) ** 300ml of desiccation tetrahydrofuran solutions which dissolved synthetic 2-BUROMO pyridine 5.5g of a 2-pyridyl-(1, 3-dimethyl-5-pyrazolyl) methanol was cooled at -78 degree C, 5.45g (15 W/W%) of n-butyl lithium hexane solutions was slowly dropped at this, and it agitated for 30 minutes. Next, 1 and 3-dimethyl-5-formyl pyrazole 4.2g was slowly dropped at -78 degree C. The temperature up was slowly carried out even to the room temperature after this, and it agitated for 15 hours.

[0072] After adding the hydrochloric acid of 2 conventions to this solution and making it neutrality, 150ml of ethyl acetate extracted 3 times. The organic layer was dried with anhydrous sodium sulfate, and 2-pyridyl-(1, 3-dimethyl-5-pyrazolyl) methanol 5.2g was obtained as brown oily matter by carrying out reduced pressure distilling off of the solvent, and refining residue with a silica gel column chromatography (developing solution; chloroform).

[0073] ** In 60ml of desiccation chloroform solutions which dissolved synthetic 2-pyridyl-(1, 3-dimethyl-5-pyrazolyl) methanol 3g of this invention compound No.99, under the room temperature, 4-chlorophenyl sulfenyl chloride 3.4g was dropped, and it agitated for 12 hours. After distilling off a solvent, 50ml of ethyl acetate and 50ml of 10% sodium-hydrogencarbonate water solutions were added, and it agitated for 30 minutes. After separating an organic layer, 50ml of ethyl acetate extracted the water layer 3 times further. The doubled organic layer was dried with anhydrous sodium sulfate, and after carrying out reduced pressure distilling off of the solvent, 2-pyridyl-(4-(4-chloro phenylthio)-1, 3-dimethyl-5-pyrazolyl) methanol 1.2g was obtained as a white crystal by refining residue with a silica gel chromatography (developing solution; chloroform). The melting point of 90.0-91.0 degrees C [0074] [The example 2 of manufacture] (composition of this invention compound No.115)

This invention compound No.99 obtained in the example 1 of manufacture In the solution which dissolved 1.2g in desiccation dichloromethane 50ml, at the room temperature, 1.5g of manganese dioxides was added and it agitated for 2 hours. After carrying out an inorganic substance a ** exception with cerite, reduced pressure distilling off of the solvent was carried out, and 2-pyridyl-(4-(4-chloro phenylthio)-1, 3-dimethyl-5-

pyrazolyl) ketone 1.0g was obtained as a white crystal by crystallizing residue with diisopropyl ether. The melting point of 111.0-113.0 degrees C [0075] [The example 3 of manufacture] (composition of this invention compound No.95)
The heating reflux of the 10ml of the 4 iodation 2 Lynn 0.5g benzene solutions was carried out for 10 minutes under the nitrogen air current. 30ml of benzene solutions which dissolved this invention compound No.99 (1.2g) obtained in the example 1 of manufacture in this solution was dropped, and heating reflux was carried out for 16 hours. 5ml of sodium-hydrogensulfite water solutions was added after [air cooling] 10%, and it agitated at the room temperature for 1 hour.
[0076] 50ml of ethyl acetate extracted this solution 3 times, and the organic layer was dried with anhydrous sodium sulfate. 4-(4-chloro phenylthio)-1 and 3-dimethyl-5-(2-pyridyl methyl) pyrazole 0.34g was obtained by carrying out reduced pressure distilling off of the solvent, and refining residue with a silica gel column chromatography (developing solution; chloroform). The melting point of 80.0-82.0 degrees C [0077] [The example 4 of manufacture] (composition of this invention compound No.22)
** The mixed solution of N-(2-pyridyl) formamide 11.4g and 20ml of N.N-dimethylformamide was dropped at 100ml of suspended N.N-dimethylformamide of 4.6g (55%) of synthetic sodium hydride of a 3-chloro-1-methyl-4-nitro-5-(2-pyridylamino) pyrazole under ice-cooling, and it agitated under the room temperature for about 1 hour. 3 Next, five - The solution which dissolved dichloro-1-methyl-4-nitro pyrazole 17.5g in 20ml of N.N-dimethylformamide was dropped under ice-cooling, and heating churning was carried out at 60 degrees C after that for 8 hours. Reduced pressure distilling off of the N.N-dimethylformamide was carried out after cooling, chloroform extracted, and the sodium-carbonate water solution washed the organic layer, and it dried with anhydrous sodium sulfate after washing in cold water continuously. Reduced pressure distilling off of the solvent was carried out after filtration, isopropyl ether washed the remaining crystal, and 3-chloro-1-methyl-4-nitro-5-(2-pyridylamino) pyrazole 14.2g of the purpose was obtained by carrying out filtration desiccation. The melting point of 127.0-129.0 degrees C [0078] ** Synthetic 3-chloro-1-methyl-4-nitro-5-(2-pyridylamino) pyrazole 7g of a 4-amino-3-chloro-1-methyl-5-(2-pyridylamino) pyrazole was added and dissolved in the mixed solution of ethanol 50ml and 50ml of concentrated hydrochloric acid. 31g of stannous chloride 2 hydrates and an ethanol 70ml mixed solution were dropped there under the room temperature, and it agitated at 80 degrees C for 7 hours. Reaction mixture was poured out after cooling and into iced water, the sodium-hydroxide water solution was added 20%, and it was made alkalinity. Ethyl acetate extracted and it dried with anhydrous sodium sulfate after washing in cold water. 4-amino-3-chloro-1-methyl-5-(2-pyridylamino) pyrazole 5.0g of the purpose was obtained as a crystal by carrying out reduced pressure distilling off of the solvent after filtration. The melting point of 151.0-153.0 degrees C [0079] ** synthetic 4-amino-3-chloro-1-methyl-5-(2-pyridylamino) pyrazole 1.5g of a 3-chloro-1-methyl-5-(2-pyridylamino) pyrazole -- the mixed solution of ethanol 50ml and 5ml of concentrated sulfuric acid -- in addition, heating reflux was carried out. 1.1g of sodium nitrites was added little by little to this solution. Generating of nitrogen gas was observed at this time. Heating reflux was carried out after addition termination of a sodium nitrite for 30 minutes. After cooling, after adding the sodium-hydroxide water solution 20% and making it alkalinity, chloroform extracted and it dried with anhydrous sodium sulfate after rinsing an organic layer. Reduced pressure distilling

off of the solvent was carried out after filtration. By refining residue with a silica gel column chromatography (developing solution; chloroform-ethyl acetate), 3-chloro-1-methyl-5-(2-pyridylamino) pyrazole 1.1g was obtained. The melting point of 105.0-106.0 degrees C [0080] ** Synthetic 3-chloro-1-methyl-5-(2-pyridylamino) pyrazole 1.05g of this invention compound No.22 was dissolved in anhydrous chloroform 30ml. 2 and 4-dichlorophenyl sulfenyl chloride 1.3g was dropped at this solution, and it agitated at the room temperature for 3 hours. After adding a sodium-carbonate water solution, chloroform extracted and it dried with anhydrous sodium sulfate after rinsing an organic layer. 3-chloro-4-(2, 4-dichloro phenylthio)-1-methyl-5-(2-pyridylamino) pyrazole 1.42g was obtained by carrying out reduced pressure distilling off of the solvent after filtration, and refining residue with a silica gel column chromatography (developing solution; chloroform). The melting point of 147.0-148.0 degrees C [0081] [The example 5 of manufacture] (this invention compound composition of No.168)
** 5-amino - Composition 3 and 5 of a 3-chloro-1-methyl-4-methoxycarbonyl pyrazole - Dichloro-1-methyl-4-methoxycarbonyl pyrazole 100g was dissolved in anhydrous dimethyl sulfoxide 350ml, sodium azide 37.3g was added continuously, and it stirred for three days at 60 degrees C. The crystal which filled 800ml of iced water with reaction mixture, and ****(ed) it was filtered, and it washed with water. By drying a crystal, it is 5-azide. - 81.5g of about 65% inclusions of a 3-chloro-1-methyl-4-methoxycarbonyl pyrazole was obtained. Anhydrous methanol 400ml and piperidine 1.5g were added to this mixture, and it cooled to about 15 degrees C by iced water. Hydrogen-sulfide gas was blown there for about 1 hour. Then, hydrogen-sulfide gas with an entrainment superfluous for about 15 minutes was removed for nitrogen gas. Except for the sulfur which is ****(ing), reduced pressure distilling off of the solvent was carried out by filtration. Chloroform 150ml and 50ml of saturation sodium-carbonate water solutions were added to residue, and it stirred for 30 minutes. It dried with anhydrous sodium sulfate after a chloroform extraction and washing in cold water. It is 5-amino as a crystal of light yellow by refining residue with a silica gel column chromatography (developing solution; chloroform-ethanol) after filtration and solvent distilling off. - 47.1g (52% of yield) of 3-chloro-1-methyl-4-methoxycarbonyl pyrazoles was obtained. Melting point 104.0-105.0 degrees C [0082] ** Synthetic 5-amino -3 of 5-amino-3-chloro-1-methyl pyrazole - In addition to the mixed water solution of methanol 200ml and 250ml of water which dissolved 31.4g of sodium hydroxides for chloro-1-methyl-4-methoxycarbonyl pyrazole 55.5g, heating reflux was performed for 3 hours. The bottom solvent of reduced pressure was distilled off after cooling. 300ml of water was added, the hydrochloric acid (31%) was added, and it was made the acidity of pH2. The crystal which ****(ed) was filtered and about 50g of white crystals of a carboxylic acid (5-amino-3-chloro-1-methyl-4-pyrazolyl) was obtained by drying after rinsing.
[0083] Next, the above-mentioned crystal was added little by little to the place which is carrying out heating stirring of the mixed water solution of 100ml (31%) of hydrochloric acids, and 50ml of water at 80 degrees C. (Generating of carbon dioxide gas was seen.) Since it finished adding a crystal, stirring was performed at 80 more degrees C for 3 hours. Then, under reduced pressure, after carrying out abbreviation one half distilling off of the water, the potassium-hydroxide water solution was added and it was made the alkalinity of the 11th place of pH. Moreover, acetonitrile 300ml was added to the place which distilled off reduced pressure sewage completely, and it dried with anhydrous

sodium sulfate and anhydrous potassium carbonate. 35g (91% of yield) of 5-amino-3-chloro-1-methyl pyrazole was obtained as a white crystal by distilling off an acetonitrile under reduced pressure after filtration. Melting point 84.0-85.0 degrees C [0084] ** 50.4g of acetic anhydrides was continuously added 27.3g of formic acid and added [dropped and] to synthetic 5-amino-3-chloro-1-methyl pyrazole 52g of a 3-chloro-1-methyl-5-(2-pyrimidyl amino) pyrazole. It stirred for two days at the room temperature. The solvent was distilled off under reduced pressure. Chloroform 160ml was added and it dried with anhydrous sodium sulfate. N-(3-chloro-1-methyl-5-pyrazolyl) formamide about 68g was obtained by distilling off a solvent after filtration. It was used for the next reaction, without refining this. The mixture of the above-mentioned N-(3-chloro-1-methyl-5-pyrazolyl) formamide 68g and 120ml of N.N-dimethylformamide was dropped and added to the solution of 400ml of suspended N.N-dimethylformamide of 21g of sodium hydride (oily 55%) under ice-cooling. 2-chloro pyrimidine 49.9g was added after 4-hour stirring at the room temperature. It stirred at 120 degrees C with the room temperature after that for 15 hours for 2 hours. It distilled off under reduced pressure of a solvent after cooling, and 200ml was added and chloroform 200ml and water were stirred at the room temperature for 2 hours. The chloroform extraction was carried out and it dried with anhydrous sodium sulfate after rinsing. After filtration, when the solvent was distilled off under reduced pressure, the brown crystal object was obtained. After adding and stirring ethanol 100ml and diethylether 100ml there, the crystal was filtered and 43g (52% of yield) of 3-chloro-1-methyl-5-(2-pyrimidyl amino) pyrazoles was obtained by drying after washing by ethanol. Melting point 146.0-148.0 degrees C [0085] ** Composition of a 3-chloro-4-(3-fluoro-4-methyl phenylthio)-1-methyl-5-(2-pyrimidyl amino) pyrazole (composition of this invention compound No.168)
3-chloro-1-methyl-5-(2-pyrimidyl amino) pyrazole 16.6g was dissolved in anhydrous chloroform 150ml, and it cooled at about about 10 degrees C by iced water. Mixed liquor (3-fluoro-4-methylphenyl sulfenyl chloride 16.1g and chloroform 10ml) was dropped and added there. It stirred at the room temperature after termination for 6 hours. 50ml of saturation sodium-carbonate water solutions was added, and they were stirred for 30 more minutes. The chloroform extraction was carried out and it dried with anhydrous sodium sulfate after rinsing. After filtration, when chloroform was distilled off under reduced pressure, the crystal was obtained. After adding and stirring diethylether 50ml and ethanol 50ml there, the crystal was carried out the ** exception and it washed by ethanol. By drying a crystal, 21.5g (77% of yield) of 3-chloro-4-(3-fluoro-4-methyl phenylthio)-1-methyl-5-(2-pyrimidyl amino) pyrazoles was obtained as a crystal of light gray. Melting point 178.0-179.0 degrees C [0086] [The example 6 of manufacture] Composition of an N-(3-chloro-4-(3-fluoro-4-methyl phenylthio)-1-methyl-5-pyrazolyl)-N-(2-pyrimidyl) formamide (this invention compound composition of No.189)
13.5g of formic acid and 30.4g of acetic anhydrides were added to 3-chloro-4-(3-fluoro-4-methyl phenylthio)-1-methyl-5-(2-pyrimidyl amino) pyrazole 25.0g, and it stirred at the room temperature for 14 hours. After carrying out reduced pressure distilling off of the solvent of reaction mixture which became homogeneity, chloroform 100ml and 100ml of water were added, and it stirred for 1 hour. The chloroform layer was washed in cold water to the extract and the pan and it dried with anhydrous sodium sulfate. Reduced pressure distilling off of the chloroform was carried out after filtration, 2ml of diisopropyl ether was added, the crystal was deposited, and it washed and filtered by normal hexane

40ml. Furthermore, it washed with mixed liquor (normal hexane 40ml and diisopropyl ether 7ml). 23.9g (88% of yield) of N-(3-chloro-4-(3-fluoro-4-methyl phenylthio)-1-methyl-5-pyrazolyl)-N-(2-pyrimidyl) formamides was obtained as a white crystal by drying this. The melting point of 91.0-92.0 degrees C [0087] [The example 7 of manufacture] (composition of this invention compound No.278)
** the mixed liquor of N-(1, 3-dimethyl-5-pyrazolyl) formamide 4g and 15ml of N.N-dimethylformamide was dropped at the solution of 100ml of suspended N.N-dimethylformamide of 1.5g (55% [ ] -- oily) of synthetic sodium hydride of a 1 and 3-dimethyl-5-(6-fluoro-2-pyridylamino) pyrazole under cooling, and was added to it. It stirred at the room temperature after dropping termination for 4 hours. 3.2g of 2 and 6-difluoro pyridines was added, and it stirred at 130 degrees C with the room temperature for 3 hours for 18 hours. The bottom solvent of reduced pressure was distilled off after cooling, the chloroform extraction of the residue was carried out, and it dried with anhydrous sodium sulfate after rinsing. The solvent was distilled off after filtration and 3.6g (65% of yield) of 1 and 3-dimethyl-5-(6-fluoro-2-pyridylamino) PIRASORU was obtained by refining residue with a silica gel column chromatography (developing solution; chloroform). The melting point of 112.0-113.0 degrees C [0088] ** 1, composition of a 3-dimethyl-4-(3-fluoro-4-methyl phenylthio)-5-(6-fluoro-2-pyridylamino) pyrazole (composition of this invention compound No.278)
1 and 3-dimethyl-5-(6-fluoro-2-pyridylamino) pyrazole 0.6g was dissolved in anhydrous chloroform 30ml, 3-fluoro-4-methylphenyl sulfenyl chloride 0.61g was added, and it stirred at the room temperature for 12 hours. 10ml of saturation sodium-carbonate water solutions was added, and they were stirred for 30 minutes. The chloroform extraction was carried out and it dried with anhydrous sodium sulfate after rinsing. 1 and 0.72g (71% of yield) of 3-dimethyl-4-(3-fluoro-4-methyl phenylthio)-5-(6-fluoro-2-pyridylamino) pyrazoles were obtained by distilling off a solvent under reduced pressure after filtration, and washing the remaining crystal with diisopropyl ether. Melting point 96.0-98.0 degrees C [0089] [The example 8 of manufacture] (composition of this invention compound No.9)
** Synthetic 5-amino -3 of 5-amino-3-methoxy-1-methyl pyrazole - In addition to the water solution of methanol 150ml and 150ml of water which dissolved 6.1g of sodium hydroxides for methoxy-1-methyl-4-methoxycarbonyl pyrazole 10.5g, overheating reflux was performed for 3 hours. After cooling, the solvent was distilled off under reduced pressure, and under ice-cooling, the hydrochloric acid was added and it considered as the acidity of pH2. Under reduced pressure, after distilling off water completely, ethanol 150ml was added and it dried with anhydrous sodium sulfate. After filtration, when ethanol was distilled off, the shape of an oil of light yellow remained. Xylene 100ml and 0.5g of copper powder were added, and heating reflux was performed for 18 hours. After filtering and removing copper powder and carrying out reduced pressure distilling off of the xylene, acetonitrile 100ml was added and it dried with anhydrous sodium sulfate. 6.67g (92% of yield) of 5-amino-3-methoxy-1-methyl pyrazole was obtained by distilling off the bottom solvent of reduced pressure after filtration.
[0090] ** 6.6g of formic acid was added to synthetic 5-amino-3-methoxy-1-methyl pyrazole 6.67g of a 3-methoxy-1-methyl-5-(2-pyrimidyl amino) pyrazole, it was followed, 16.2g of acetic anhydrides was dropped and, in addition, they were stirred for three days at the room temperature. The bottom solvent of reduced pressure was distilled

off, 100ml of chloroform was added, and it dried with anhydrous sodium sulfate. When after [filtration] vacuum concentration was carried out, 9.7g of crude objects of N-(3-methoxy-1-methyl-5-pyrazolyl) formamide was obtained. The next reaction was performed without refining. in addition, the mixed liquor of the above-mentioned N-(3-methoxy-1-methyl-5-pyrazolyl) formamide 9.7g and 50ml of N,N-dimethylformamide was dropped and stirred at the room temperature for 4 hours to 150ml of N,N-dimethylformamide which made 3.3g (55% [ ] -- oily) of sodium hydride suspend. Then, 2-chloro pyrimidine 7.9g was added and it stirred at 100 degrees C for 18 hours. The chloroform extraction of the residue which carried out vacuum concentration was carried out after cooling, and it dried with anhydrous sodium sulfate after rinsing. The solvent was distilled off after filtration and 2.6g (24% of yield) of 3-methoxy-1-methyl-5-(2-pyrimidyl amino) pyrazoles was obtained as oil by refining residue with a silica gel column chromatography (developing solution; chloroform).

[0091] ** Composition of a 4-(3-chloro-4-methyl phenylthio)-3-methoxy-1-methyl-5-(2-pyrimidyl amino) pyrazole (composition of this invention compound No.9)

3-methoxy-1-methyl-5-(2-pyrimidyl amino) pyrazole 0.7g was dissolved in anhydrous chloroform 30ml, 3-chloro-4-methylphenyl sulfenyl chloride 0.65g was added, and it stirred at the room temperature for 18 hours. The saturation sodium-carbonate water solution was added, and the chloroform extraction was carried out after stirring for 30 minutes at the room temperature, and it dried with anhydrous sodium sulfate after rinsing. The solvent was distilled off after filtration and 0.57g (51% of yield) of 4-(3-chloro-4-methyl phenylthio)-3-methoxy-1-methyl-5-(2-pyrimidyl amino) pyrazoles was obtained by refining residue with a silica gel column chromatography (developing solution; chloroform). Melting point The physical properties of the compound manufactured according to these approaches 148.0-150.0 degrees C are shown in the 2nd table.

[0092] ** 2 Table [0093]

[Table 14]

---------- A compound 1 H-NMR No. Object Sex delta (ppm and CDCl3) and the standard substance TMS ---------- 1 m.p.168.0 - 169.0 ** 2 m.p.175.0 - 176.0 ** 3 m.p.162.0 - 163.0 ** 4 m.p. 91.0 to 93.0 ** 5 m.p.184.0-185.0 **6 m.p.172.0 - 174.0 ** 7 m.p.179.0 - 181.0 ** 9 m.p.148.0-150.0 ** 10 m.p.209.0 - 210.0 ** 11m.p.137.0 - 138.0 ** 12 m.p.153.0 - 155.0 ** 15 m.p.209.0 - 212.0 ** 16 m.p.168.0 - 170.0 ** 17 m.p. 92.0 - 95.0 ** 18 m.p.136.0-138.0 ** 19 m.p.120.0-124.0 ** 20m.p.177.0 - 180.0 ** 21 m.p.157.0 - 159.0 ** 22 m.p.147.0-148.0 ** 95 m.p. 80.0 to 82.0 ** 96 m.p. 88.0 - 89.0 ** ---------- ---------- [0094]

[Table 15]

** 2 Table (continuation)

---------- A compound 1 H-NMR No. Object Sex delta (ppm and CDCl3) and the standard substance TMS ---------- 99 m.p. 90.0 to 91.0 ** 100 m.p.142.0-145.0 ** 104 The shape of resin 2.20 (s, 6H), 3.55 (s, 3H), 5.10 (bs, 1H), 6.05 (s, 1H) and 6.50- 7.60 (m, 6H) and 8.40 (d, 1H, J= 5Hz) 105 Oily matter 2.17 (s, 3H), 3.30 (s, 3H), and 3.68 (s, 3H) -- 5.68 (s, 1H), 6.80-7.70 (m, 7H) 8.30-8.50 (m, 1H) 107 Oily matter 2.10 (s, 3H), 2.25 (s, 3H), 4.05 (s, 3H), 6.80-8.70 (m, 9H) 111 Oily matter 2.19 (s, 3H), 3.77 (s, 3H), 6.67 (d, 1H, J= 45Hz) 6.90-7.70 (m, 7H), 8.51 (d, 1H, J= 5Hz) 115m.p.111.0-113.0 ** 119 Oily matter 2.03 (s, 3H), 2.16 (s, 3H), 3.69 (s, 3H), 6.00 (bs, 1H) 6.80-8.51 (m, 8H) 127 The shape of resin 0.50 (d, 3H, J= 7Hz) 1.00 (d, 3H, J= 7Hz),

2.02 (s, 3H), 3.21-3.65 (m, 1H), 3.87 (s, 3H), 6.00 (bs, 3H) 6.61-8.35 (m, 8H) 131 Oily matter 1.71 (d, 3H, J= 7Hz), 2.17 (s, 3H), 3.73 (s, 3H), 4.69 (q, 1H, J= 7Hz), 6.70-7.60 (m, 7Hz) 8.30-8.50(m, 1H) ---------- [0095]
[Table 16]
** 2 Table (continuation)
---------- A compound 1 H-NMR No. Object Sex delta (ppm and CDCl3) and the standard substance TMS ---------- 145 m.p.218.0-220.0 ** 155 m.p.121.0-122.0 ** 167 m.p.174.0-175.0 ** 168 m.p.178.0-179.0 ** 169m.p.157.0-159.0 ** 170 m.p.156.0-157.0 ** 171 m.p.159.0-160.0 ** 172 m.p.184.0-186.0 ** 173 m.p.179.0-180.0 ** 174 m.p.186.0-187.0 ** 175 m.p.172.0-173.0 ** 176 m.p.172.0-174.0 ** 177 m.p.154.0-155.0 ** 178 m.p.136.0 - 139.0 ** 179 m.p.167.0-168.0 ** 180 m.p.144.0-145.0 ** 181 m.p.132.0-133.0 ** 182 m.p.144.0-145.0 ** 183 m.p.132.0-133.0 ** 184 m.p.149.0-150.0 ** 185 m.p.143.0 - 144.0 ** ---------- [0096]
[Table 17]
** 2 Table (continuation)
---------- A compound 1 H-NMR No. Object Sex delta (ppm and CDCl3), the standard substance TMS ---------- 186 m.p.140.0-141.0 ** 187 m.p. 90.0- 91.0 ** 188 Oily matter 189 m.p. 91.0 - 92.0 ** 190 The shape of resin 191 Oily matter 263 m.p.153.0-154.0 ** 264 m.p.117.0-119.0 ** 265 m.p.108.0-110.0 degree C 266 m.p.116.0-118.0 ** 270 Oily matter 271 m.p.183.0-184.0 ** 275 m.p.172.0-174.0 ** 276 m.p.104.0-106.0 ** 277 m.p.142.0-144.0 ** 278 m.p. 96.0 - 98.0 ** ---------- In using this invention compound as a germicide for plantation arts Generally A solid support or water, such as suitable support, for example, clay, talc, vent NANTO, and diatomaceous earth, alcohols and aromatic hydrocarbon (a methanol, ethanol, etc.) (benzene --) Chlorinated hydrocarbon, such as toluene and a xylene, ether, and ketones It can use with liquid support, such as ester (ethyl acetate etc.) and acid amides (dimethylformamide etc.), together, and can apply. An emulsifier, a dispersant, suspension, a penetrating agent, a spreader, a stabilizer, etc. can be added by request, and practical use can be presented in the pharmaceutical form of arbitration, such as liquids and solutions, oils, an emulsion, water dispersible powder, powder material, a granule, and a floor bull agent.
[0097] Moreover, mixed use may be carried out if needed with the herbicide of other type, various insecticides, a germicide, a plant growth regulator, a synergist, etc. at the time of pharmaceutical preparation or spraying. Although it is different with an application scene, a use stage, the use approach, object disease, cultivation crops, etc., generally about 0.005-50kg per hectare is suitable for the use dose of this invention compound as an amount of active principles. Next, although the example of pharmaceutical preparation of the germicide which makes this invention compound an active principle is shown, they are not these things limited to seeing. In addition, in the following examples of pharmaceutical preparation, the "section" means the weight section.
[0098] Example 1 of pharmaceutical preparation Milk Agent this invention compound ---------- 20 Section xylene -------- 55 Section N.N-dimethylformamide ------- 20 Section SORUPORU 2680 --------- 5 Section (mixture of a nonionic surfactant and an anionic surfactant: Toho Chemical Industry Co., Ltd. trade name)

It mixes to homogeneity and let the above be an emulsion. On the occasion of use, the above-mentioned emulsion is diluted 50 to 20000 times, and the amount of active principles is per hectare. It sprinkles so that it may be set to 0.005-50kg.
[0099] Example 2 of pharmaceutical preparation Water-dispersible-powder this invention compound -------- 25 Section JIKU light PFP -------- 66 Section (a kaolinite and mixture of a sericite; JIKU RAITO KOGYO CO., LTD. trade name)
SORUPORU 5039 ------- 4 Section (anionic surfactant: Toho Chemical Industry Co., Ltd. trade name)
Carplex #80 ------- 3 Section (white carbon: Shionogi& Co., Ltd. trade name)
ligninsulfonic acid calcium ------- 2 Preferential grinding more than of the section is carried out to homogeneity, and it considers as water dispersible powder. On the occasion of use, the above-mentioned water dispersible powder is diluted 50 to 20000 times, and the amount of active principles is per hectare. It sprinkles so that it may be set to 0.005-50kg.
[0100] Example 3 of pharmaceutical preparation Oil Agent this invention compound ---------- 10 Section methyl Cellosolve -------- 90 It mixes to homogeneity and let more than the section be oils. Use is faced and the amount of active principles is the above-mentioned oils per hectare. It sprinkles so that it may be set to 0.005-50kg.
[0101] Example 4 of pharmaceutical preparation Powder Agent this invention compound ------- 3.0 section Carplex #80 ------- The 0.5 sections (white carbon: Shionogi& Co., Ltd. trade name)
Clay ------- 95 Section phosphoric-acid diisopropyl ------- Preferential grinding of the 1.5 or more sections is carried out to homogeneity, and it considers as powder material. Use is faced and the amount of active principles is the above-mentioned powder material per hectare. It sprinkles so that it may be set to 0.005-50kg.
[0102] example 5 of pharmaceutical preparation Grain Agent this invention compound ---------- 5 Section bentonite ------- 54 Section talc ------- 40 section ligninsulfonic acid calcium ------- 1 Preferential grinding more than of the section is carried out to homogeneity, little water is added and churning mixing is carried out, and it corns and dries with an extrusion type granulating machine, and considers as a granule. Use is faced and the amount of active principles is the above-mentioned granule per hectare. It sprinkles so that it may be set to 0.005-50kg.
[0103] Example 6 of pharmaceutical preparation Floor bull agent this invention compound ------- 25 Section SORUPORU 3353 ------- 10 Section (nonionic surfactant: Toho Chemical Industry Co., Ltd. trade name)
RUNOKKUSU 1000C ------- 0.5 Section (anionic surfactant: Toho Chemical Industry Co., Ltd. trade name)
1% xanthan gum water solution ------- 20 Section (naturally-ocurring polymers)
Water ------- The above-mentioned component except a 44.5 section active principle (this invention compound) is dissolved in homogeneity, after being easy to add this invention compound and agitating it subsequently, wet grinding is carried out in a sand mill, and a floor bull agent is obtained. On the occasion of use, the above-mentioned floor bull agent is diluted 50 to 20000 times, and the amount of active principles is per hectare. It sprinkles so that it may be set to 0.005-50kg.
[0104] next, as plant disease set as the object of this invention compound the rice blast (Pyricularia oryzae) of a rice, and Cochliobolus miyabeanus (Cochliobolus miyabeanus)

Rhizoctonia solani (Rhizoctonia solani) Japanese noodles **** of wheat (Erysiphe graminis f.sp.hordei, f.sp.tritici) Pyrenophora graminea (Pyrenophora graminea) Pyrenophora teres (Pyrenophora teres), a red mold disease (Gibberella zeae) and rust (Puccinia striiformis, P.graminis, P.recondita, P.hordei) Snow mould (Typhula sp., Micronectriella nivais), nakedness smut (Ustilago tritici, U.nuda) An ice pot (Pseudocercosporella herpotrichoides), Cloud form disease (Rhynchosporium secalis) Septoria tritici (Septoria tritici), Leptosphaeria nodorum (Leptosphaeria nodorum), [0105] Sunspot disease of a citrus (Diaporthe citri) Scab (Elsinoe fawcetti), fruits rot (Penicillium digitatum, P.italicum) moniliasis of an apple (Sclerotiniamali) Illness not rotting (Valsa mali) Japanese noodles **** (Podosphaera leucotricha) spot fallen-leaves disease (Alternaria mali) Black spot (Venturia inaequalis) the black spot (Venturia nashicola) of a pear, and black rot (Alternaria Kikuchiana) Gymnosporangium japonicum (Gymnosporangium haraeanum), The brown rot (Sclerotinia cinerea) of a peach, and a black spot (Cladosporium carpophilum), Phomopsis rot (Phomopsis sp.) and the downy mildew (Plasmopara viticola) of a grape, black and **** (Elsinoe ampelina) Glomerella cingulata (Glomerella cingulata) Japanese noodles **** (Uncinula necator) and rust (Phakopsora ampelopsidis) ****** of an oyster (Gloeosporium kaki) A fallen-leaves disease (Cercospora kaki, Mycosphaerella nawae) and [0106] The downy mildew of melons (Pseudoperenospora cubensis), ******* (Colletotrichum lagenarium) Japanese noodles **** (Sphaerotheca fuliginea) Mycosphaerella melonis (Mycosphaerella melonis), The epidemic (Phytophthora infestans) of a tomato, Ring spot (Alternaria solani) A leaf mold disease (Cladosporium fulvam), Phomopsis vexans of an eggplant (Phomopsis vexans) Japanese noodles **** (Erysiphe cichoracoarum) The black rot of the Brassicaceae vegetables (Alternariajaponica), The white spot disease (Cerocosporella brassicae), the rust of a Welsh onion (Puccinia allii), purpura of soybeans (Cercospora kikuchii) Black and **** (Elsinoe glycines) sunspot disease (Diaporthe phaseololum) ****** of a kidney bean (Colletotrichum lindemuthianum) Cercospora personata of a peanut (Mycosphaerella personatum) Cercospora leaf spot (Cercospora arachidicola) and Japanese noodles **** of a pea (Erysiphe pisi) [0107] Leaf blight of a potato (Alternaria solani) Japanese noodles **** (Sphaerothecahumuli) of a strawberry, network rice cake disease of tea (Exobasidium reticulatum) elsinoe leucospila (Elsinoe leucospila) and Gymnosporangium japonicum of tobacco (Alternaria longipes) Japanese noodles **** (Erysiphe cichoracearum) ****** (Colletotrichum tabacum) Cercospora leaf spot of a sugarbeet (Cercospora beticola) Rose black spot (Diplocarpon rosae) Japanese noodles **** (Sphaerotheca pannosa), Cercospora leaf spot of a chrysanthemum (Septoria chrysanthemiindici) white rust (Puccinia horiana) Gray mold disease of various crops (Botrytis cinerea) Sclerotinia rot (Sclerotinia sclerotiorum) etc. -- it is mentioned. The usefulness of this invention compound is concretely explained in the following examples of a trial. However, they are not these things limited to seeing.

[0108] Example 1 of a trial To the cucumber (form: the Sagami half white) of one to 2 leaf stage raised by the pot with a gray mold disease prevention effectiveness trial diameter of 7cm, this invention compound emulsion is diluted with water, and it is 500 ppm. A spray gun is used for the prepared drug solution, and it is 20 ml per pot. It sprinkled. The leaf was cut off from the cucumber which sprinkled the drug solution on the next day [spraying], and it placed into the bat which covered with the paper in which water was included. It is cucumber gray mold contagion (Botrytis cinerea) to this. The

spray inocuration of the spore suspension (a 1.0 % glucose, 2.5 % yeast extract content, x 150.40 piece /, visual field) was carried out. After inoculation, the bat was covered with vinyl and put on the thermostatic chamber with a temperature of 18 degrees C for five days. The formed necrotic lesion diameter was measured and preventive value was computed according to the following formula.

Preventive value =[1-(processing division necrotic lesion diameter (mm) / non-processed division necrotic lesion diameter (mm))] x100, consequently the following compounds showed preventive value 100.

This invention compound No1 No2 No3 No4 No6 No9 No11, No12, No21, No22, No95, No96, and No111, No131, No167, No168, No169, and No170, No171, No172, No173, No174, and No175, No176, No177, No178, No180, and No181, No182, No183, No185, No186, No188, No189, No190, No191, No263, No264, No265, No266, No276, No277, No278 [0109] Example 2 of a trial To the rice (form: Japanese fine) of three to 4 leaf stage raised by the pot with a rice-sheath-blight-disease prevention effectiveness trial diameter of 5cm, this invention compound emulsion is diluted with water, and it is 500 ppm. It is 5ml about the prepared drug solution. It is 15 ml per pot to the same pot immediately after carrying out the stock former douche. It sprinkled. The Rhizoctonia solani (Rhizoctonia solani) contamination **** was placed and inoculated into stock origin three days after processing. After that, the pot was put on the temperature of 28 degrees C, and the inoculation chamber beyond humidity 95%, the height from **** of the necrotic lesion formed five days after inoculation was measured, and preventive value was computed according to the following formula.

preventive value =[1-(processing division necrotic lesion quantity / non-processed division necrotic lesion quantity)] x100 -- as a result, the following compounds showed preventive value 100.

This invention compound No1 No2 No3 No6 No7 No9 No11, No12, No17, No21, No22, No95, No96, No99, and No100, No104, No105, No111, No115, and No167, No168, No169, No170, No171, and No172, No173, No174, No175, No176, and No178, No179, No180, No181, No182, and No183, No184, No185, No186, No187, No189, No190, No191, No263, No275, No276, No277, No278 [0110]

[Effect of the Invention] this invention compound is a new compound, and since the outstanding germicidal action for plantation arts is shown and the phytotoxicity over useful crops is not accepted, either, it is useful as a germicide for plantation arts.

[Translation done.]

TECHNICAL FIELD

[Industrial Application] This invention relates to the germicide for plantation arts which contains a new pyrazol derivative and this derivative as an active principle.

PRIOR ART

[Description of the Prior Art] Although the germicide of former versatility has been developed, it cannot be said to be what it should not necessarily be satisfied with the effect, appearance of resistant bacteria, etc. of. Moreover, publication number 1-125379 It is indicated by a number official report, EP-459333A1, and JP,3-141276,A that a certain kind of pyrazol derivative has sterilization activity.

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention] this invention compound is a new compound, and since the outstanding germicidal action for plantation arts is shown and the phytotoxicity over useful crops is not accepted, either, it is useful as a germicide for plantation arts.

[Translation done.]

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] Also in the compound indicated by the above-mentioned open official report, it should not be satisfied in respect of effect, residual effectiveness, phytotoxicity, etc., and development of the still more useful germicide for plantation arts is demanded to plant disease.

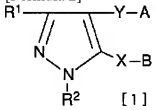
[Translation done.]

MEANS

[Means for Solving the Problem] As a result of repeating examination variously that this invention persons should develop the compound which has the outstanding sterilization

activity in view of such a situation, the permutation pyrazol derivative shown by the following formula [1] resulted having the outstanding sterilization activity in header this invention. That is, this invention is formula [1]: [0005].

[Formula 2]



[1]

[0006] R1 expresses a halogen atom, an alkyl group, an alkoxy group, an alkylthio group, or a halo alkyl group among the [above-mentioned type. R2 An alkyl group or a halo alkyl group is expressed. X - N(R3)-, -CO-, or -C (R4) (R5) - It expresses. R3 A hydrogen atom, an alkyl group, a halo alkyl group, an alkenyl radical, an alkynyl group, and -COR6 -SO two R7 is expressed. Or R4 and R5 A hydrogen atom, a halogen atom, an alkyl group, a halo alkyl group, an alkenyl radical, an alkynyl group, or -OR8 is expressed independently, respectively. R8 A hydrogen atom, an alkyl group, a halo alkyl group, an alkenyl radical, an alkynyl group, An alkoxyalkyl group, a cyano alkyl group, an alkyl carbonyl alkyl group, The phenyl alkyl group and -COR6 which have an alkoxy carbonyl alkyl group, no permuting, or a substituent -SO two R7 is expressed. Or R6 The phenyl group which has a hydrogen atom, an alkyl group, a halo alkyl group, no permuting, or a substituent, The phenyl alkyl group, the alkoxy group, or -N (R9) which has no permuting or a substituent (R10) It expresses. R7 the phenyl group or -N (R9) (R10) which has an alkyl group, a halo alkyl group, no permuting, or a substituent expressing -- R9 and R10 The phenyl group which has a hydrogen atom, an alkyl group, no permuting, or a substituent independently, respectively is expressed. Y an oxygen atom, -S-, and -SO- or -- -SO2- is expressed, A expresses the phenyl group which has no permuting or a substituent, and B expresses the heterocycle radical which has no permuting or a substituent. However, for R1, X is -N (R3) at an alkyl group. - Except for the case of non-permuted 2-pyridyl radical, non-permuted 2-pyrimidyl radical, or non-permuted 2-pyrazyl radical in B.] It is related with the germicide for plantation arts which comes out and contains the permutation pyrazol derivative expressed or its salt, and this derivative as an active principle.

[0007] In this invention, the substituent in the above-mentioned formula has following semantics. A halogen atom means a fluorine, chlorine, a bromine, and iodine, and shows a fluorine, chlorine, and a bromine preferably. The carbon number of the alkyl of an alkyl group, an alkoxy group, and an alkylthio group 1-6 are meant, respectively. For example, methyl, ethyl, n-, or i-propyl, n-, s-, i- or t-butyl, pentyl, hexyl, methoxy, Ethoxy **n- or i-propoxy, n-, s-, i- or t-butoxy, pentoxy, HEKISOKISHI, methylthio, ethyl thio, n- or i-propyl thio, n-, s-, i-, or t-butyl thio is mentioned. Preferably, methyl, ethyl, n- or i-propyl, n-, s-, i- or t-butyl, methoxy, and ethoxy **n- or i-propoxy, n-, s-, i-, or t-butoxy is mentioned.

[0008] The carbon number of the alkyl of a halo alkyl group means 1-6, for example, fluoro methyl, difluoromethyl, trifluoromethyl, chloromethyl, bromomethyl, trifluoroethyl, trichloroethyl, trifluoro propyl, etc. are mentioned. or [that the number of the substituents of the phenyl group which has a substituent is 1-5, and the class of the

substituent is the same] -- or it may be different from each other. The phenyl group permuted as the substituent by a halogen atom, an alkyl group, a halo alkyl group, the alkoxy group, the alkylthio group, the nitro group, the cyano group, etc. is mentioned. however, n under above-mentioned definition -- normal -- in i, s expresses SEKANDARI and t expresses tertiary for ISO.

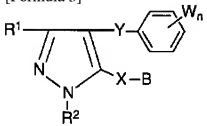
[0009] The heterocycle expressed with the above-mentioned B expresses the condensation heterocycle containing 5, 6 membered-ring heterocycle, or one or more nitrogen atoms containing one or more nitrogen atoms, for example, a pyridine, a pyrimidine, pyridazine, pyrazine, triazine, a pyrrole, a pyrazole, an imidazole, a thiazole, oxazole, etc. are mentioned. As the substituent, a halogen atom, an alkyl group, an alkoxy group, a halo alkyl group, a haloalkoxy radical, etc. are mentioned.

[0010] R1 As a substituent, it is a low-grade alkyl group or a halogen atom preferably, and a halogen atom is expressed more preferably. R2 As a substituent, an alkyl group is expressed preferably. -S- is expressed, X expresses -N(R3)- preferably, and Y is R3. A hydrogen atom or -CHO is expressed preferably. A expresses preferably the phenyl group which has more than a kind of the substituent chosen from the halogen atom, the alkyl group, and the halo alkyl group, and B expresses preferably the pyrimidyl radical which has a halogen atom as the pyridyl radical which has a halogen atom as no permuting or a substituent, no permuting, or a substituent.

[0011] Next, this invention compound expressed with a formula [1] is shown in the 1st table. However, this invention compounds are not these things limited to seeing. Compound No. It is referred to in a next publication. In addition, Ph in each table About a phenyl group, it is i. About ISO, it is t. Et shows an ethyl group and Pr shows a propyl group for tertiary.

[0012] ** 1 Table [0013]

[Formula 3]



[0014] It comes out, it sets to the compound expressed, and is [0015].

[Table 1]

---------- Compound No. R1 R2 X Y Wn B ---------- 1 Cl CH3 NH S 4-Cl B1 2 Cl CH3 NH S 2 4-Cl2 B1 3 Cl CH3 NH S 3-Cl, 4-CH3 B1 4 Cl CH3NCHO S 4-Cl B1 5Cl(s) CH3 NH S 4-CH3 B1 6 Cl CH3NH S 2, 4-Cl2B1 7 Cl CH3 NHS2, 3-Cl2 B1 8 CH3O CH3 NH S 4-Cl B1 9 CH3O CH3 NH S 3-Cl, 4-CH3 B1 10 CH3O CH3 NH S 2, 4-Cl two B1 11CH(s)3O CH3 NH S 2-F, 4-CH3 B1 12 CH3O CH3 NH S 3-F, 4-CH3 B1 13 CH3OCH3 NCHO S 2 4-Cl2 B1 14 CH3O CH3 NCHO S 3-Cl, 4-CH3 B1 15 CH3S CH3 NH S 4-Cl B1 16 CH3S CH3 NH S 3 4-Cl2 B1 17CH(s)3S CH3 NH S 2 4-Cl2 B1 18 CH3S CH3 NH S 3-Cl, 4-CH3 B1 19 CH3S CH3 NH S 2-Cl, 4-CH3 B1 20CH(s)3S CH3 NH S 3-F, 4-CH three B121 Cl CH3 NH S 4-Cl B-2 22 ClCH3 NH S 2 4-Cl2 B-2 23 ClCH3 NCH3 S 4-Cl B1 ---------- [0016]

[Table 2]

** 1 Table (continuation) ---------- Compound No. R1 R2 X Y Wn B ---------- 24 Cl CH3 NCH3 S 2 4-Cl2 B1 25 Cl CH3 NCH3 S 3-Cl, 4-CH3 B1 26 Cl CH3 NEt S 4-Cl B1 27Cl(s) CH3 N-i-Pr S4-CH3 B1 28 Cl Et NH S 2 4-Cl2 B1 29 Cl i-PrNH S 2 4-Cl2 B1 30Cl(s) CHF2 NH S 4-Cl B1 31 Cl CHF2 NH S 3-Cl, 4-CH3 B1 32 Cl CF3 NHS 2, 4-Cl2 B1 33 Cl CF3 NHS 2-F, 4-CH3 B1 34 Cl CH3 NSO2CH3 S 3-F, 4-CH3 B1 35 Cl CH3 NSO2CH3 S 2 4-Cl2 B1 36 ClCH3 NSO2CH3 S 3-Cl, 4-CH3 B1 37Cl(s) CH3 NCH3S 3-Cl, 4-CH3 B-2 38Cl(s) CH3 NEt S 4-Cl B-2 39 Cl CH3 N-i-Pr S 4-CH3 B-2 40Cl Et NH S 2 4-Cl2 B24l Cl i-Pr NH S 2 4-Cl2 B-2 42 ClCHF2 NH S 4-Cl B-2 43 Cl CHF2 NH S 3-Cl, 4-CH3 B-2 44 Cl CF3 NHS 2 4-Cl2 B-2 45Cl CF3 NH S 2-F, 4-CH3 B-2 ---------- [0017]

[Table 3]

** 1 Table (continuation) ---------- Compound No. R1 R2 X Y Wn B ---------- 46 Cl CH3 NSO2CH3 S 3-F, 4-CH3 B-2 47 Cl CH3 NH S 4-Cl B3 48 Cl CH3 NH S 2 4-Cl2 B3 49Cl(s) CH3 NHS 3-Cl, 4-CH3 B4 50 Cl CH3 NH S 4-Cl B4 51 Cl CH3 NH S 4-CH3 B5 52Cl CH3 NH S 2 4-Cl2 B5 53 Cl CH3NHS 2 4-Cl2 B6 54 Cl CH3 NH S 4-Cl B6 55 Cl CH3 NH S 3-Cl, 4-CH3 B7 56 Cl CH3 NH S 2 4-Cl2 B7 57 Cl CH3 NH S 2-F, 4-CH3 B8 58 Cl CH3 NH S 3-F, 4-CH3 B9 59 Cl CH3 NH S 2 4-Cl2 B10 60 Cl CH3 NH S 3-Cl, 4-CH three B11 61 Cl CH3 NH S 3-Cl, 4-CH3 B12 62 Cl CH3 NH S 4-Cl B13 63 Cl CH3 NH S 4-CH3 B14 64 Cl CH3 NH S 2 4-Cl2 B15 65 Cl CH3 NH S 2 4-Cl2 B16 66 Cl CH3NH S 4-Cl B16 67 ClCH3 NH S 3-Cl, 4-CH3 B17 ---------- [0018]

[Table 4]

** 1 Table (continuation) ---------- Compound No. R1 R2 X Y Wn B ---------- 68 Cl CH3 NH S 2 4-Cl2 B17 69 Cl CH3 NH S 2-F, 4-CH3 B18 70 Cl CH3 NH S 3-F, 4-CH3 B18 71 CH3 CH3 CH2 S4-Cl B1 72 CH3 CH3 CH2 S 2 4-Cl2 B1 73 CH3 CH3CH2 S 2-Cl, 4-CH3 B1 74 CH3CH3 CH2 S 2-F, 4-CH three B175 CH3 CH3 CH (OH) S 4-Cl B1 76 CH3 CH3 CH (OH) S 2 4-Cl2 B1 77 CH3 CH3 CH (OH) S 2-Cl, 4-CH3 B1 78 CH3 CH3 CH (OH) S 3-Cl, 4-CH3 B1 79 CH3 CH3 CH (OH) S 2-F, 4-CH3 B1 80 CH3 CH3 CH (OH) S 3-F, 4-CH3 B1 81 CH3 CH3 CH (OCH3) S 4-Cl B1 82 CH3 CH3 CH (OCH3) S 2 4-Cl two B1 83 CH3 CH3 CH (OCOCH3) S 4-Cl B184 CH3 CH3 CH (OCOCH3) S 2 4-Cl2 B1 85CH3 CH3 CH (OCOCH3) S 2-Cl, 4-CH3 B1 86 CH3 CH3 CH (OCOCH3) S 2-F, 4-CH three B1 87 CH3 CH3 CH (F) S 4-Cl B1 88 CH3 CH3 CH (F) S 2 4-Cl2 B1 89CH3 CH3 CH (Cl) S 4-ClB1 ---------- ---------- [0019]

[Table 5]

** 1 Table (continuation) ---------- Compound No. R1 R2 X Y Wn B ---------- 90 CH3 CH3 CH (Cl) S 2 4-Cl2 B1 91 CH3 CH3 C=O S 4-Cl B1 92 CH3 CH3 C=O S 2 4-Cl2 B1 93 CH3 CH3 C=O S2-Cl, 4-CH3 B1 94CH(s)3 CH3 C=O S 2-F, 4-CH three B1 95 CH3 CH3 CH2 S 4-Cl B-2 96CH3 CH3 CH2 S2, 4-Cl2 B-2 97 CH3 CH3 CH2 S 2-Cl, 4-CH3 B-2 98 CH3CH3 CH2 S 2-F, 4-CH3 B-2 99 CH3 CH3 CH (OH) S 4-Cl B-2 100 CH3 CH3 CH (OH) S 2 4-Cl2 B-2 101 CH3 CH3 CH (OH) S 2-Cl, 4-CH3 B-2 102 CH3 CH3 CH (OH) S 3-Cl, 4-CH3 B-2 103 CH3 CH3 CH (OH) S 2-F, 4-CH3 B-2 104 CH3 CH3 CH (OH) S 3-F, 4-CH3 B-2 105 CH3 CH3 CH (OCH3) S 4-Cl B-2 106 CH3 CH3 CH (OCH3) S 2, 4-Cl2B2 107 CH3 CH3 CH (OCOCH3) S 4-Cl B-2 108 CH3 CH3 CH (OCOCH3) S 2 4-Cl2 B-2 109 CH3 CH3 CH (OCOCH3) S 2-Cl, 4-CH3 B-2 110 CH3 CH3 CH (OCOCH3) S2-F, 4-CH3 B-2 111

CH3 CH3 CH (F) S 4-Cl B-2 ---------- [0020]
[Table 6]
** 1 Table (continuation) ---------- Compound No. R1 R2 X Y Wn B ---------- 112 CH3 CH3 CH (F) S 2 4-Cl2 B2113 CH3 CH3 CH (Cl) S 4-Cl B2114 CH3 CH3 CH (Cl) S 2 4-Cl2 B2115 CH3 CH3 C=OS 4-Cl B2116 CH3 CH3 C=OS 2 4-Cl2 B2117 CH3 CH3 C=O S 2-Cl, 4-CH3 B2118 CH3 CH3 C=O S 2-F, 4-CH3 B2119 CH3 CH3 C (CH3) (OH) S 4-Cl B2120 CH3 CH3 C (CH3) (OH) S 2 4-Cl2 B2121CH3 CH3 C (CH3) (OCOCH3) S 4-Cl B2122 CH3 CH3 C (CH3) (OCOCH3) S 2 4-Cl2 B2123 CH3 CH3 C (CH3) (F) S 4-Cl B2124 CH3 CH3 C (CH3) (F) S 2 4-Cl2 B2125CH3 CH3 C (Et), (OH) S 4-Cl B2126 CH3 CH3 C (Et) and (OH) S 2 4-Cl2 B2127 CH3 CH3 C (i-Pr) (OH) S 4-Cl B2128 CH3 CH3 C (i-Pr) (OH) S2 and 4-Cl2 B2129 CH3 CH3 C (i-Pr) (OH) S 2-Cl, 4-CH3 B2130 CH3 CH3 C (i-Pr) (OH) S 2-F and 4-CH3 B2131 CH3 CH3 CH (CH3) S 4-Cl B2132CH3 CH3 CH (CH3) S 2 4-Cl2 B2133CH3 CH3 CH (CH3) S 2-Cl, 4-CH3 B-2 ---------- [0021]
[Table 7]
** 1 Table (continuation) ---------- Compound No. R1 R2 X Y Wn B ---------- 134 CH3 CH3 CH (CH3) S 2-F, 4-CH3 B-2 135 Cl CH3 CH2 S 4-Cl B-2 136 Cl CH3 CH2 S 2 4-Cl2 B-2 137 Cl CH3 CH2 S 2-Cl, 4-CH3 B-2 138 Cl CH3 CH2 S 2-F, 4-CH3 B-2 139 CH3O CH3 CH2 S 4-Cl B-2 140 CH3O CH3 CH2 S 2, 4-Cl2 B-2 141 CH3O CH3 CH2 S 2-Cl, 4-CH3 B-2 142CH3O CH3 CH2 S 2-F, 4-CH3 B-2 143 CH3 CH3 NH S 4-Cl B19 144 CH3 CH3 NH S2-Cl B19 145 CH3 CH3 NH S 2 4-Cl2 B19 146 CH3 CH3 NH S 3-Cl, 4-CH3 B19 147 CH3 CH3 NH S 2-Cl, 4-CH3 B19 148 CH3 CH3 NH O 4-Cl B20 149CH3 CH3 NH S 2-Cl B20 150 CH3 CH3 NH S 2, 4-Cl2B20 151 CH3 CH3 NH S 3-Cl, 4-CH3 B20 152 CH3 CH3 NH S2-Cl, 4-CH3 B20 153 CH3 CH3 NCHO S 4-Cl B19 154 CH3 CH3 NCHO S 2-Cl B19 155 CH3 CH3NCHO S 2 4-Cl2 B19 ---------- [0022]
[Table 8]
** 1 Table (continuation) ---------- Compound No. R1 R2 X Y Wn B ---------- 156 CH3 CH3 NCHO S 3-Cl, 4-CH3 B19 157 CH3 CH3 NCHO S 2-Cl, 4-CH3 B19 158 CH3 C2H5 NH S 4-Cl B19 159 CH3 C2H5 NH S 2-Cl B19 160 CH3 C2H5 NH S 2 4-Cl2 B19 161CH3 C2H5 NH S 3-Cl, 4-CH3 B19 162 CH3 C2H5 NH S 2-Cl, 4-CH3 B19 163 CH3 C2H5 NH S 2-F, 4-CH3 B19 164 CH3 C2H5 NH S 3-F, 4-CH three B19 165 CF3 CH3 NH S 2 4-Cl2 B19 166 CF3 CH3 NH S 2, 4-Cl2B20 167 Cl CH3 NH S 3 4-Cl2 B1 168 Cl CH3 NH S 3-F, 4-CH3 B1 169 Cl CH3 NH S 3-Cl, 4-F B1 170 Cl CH3 NH S 3-F, 4-OCH3 B1 171 Cl CH3NH S 3-Cl, 4-OCH three B1 172 ClCH3 NH S 2-Cl, 4-CH3 B1 173 Cl CH3NH S 2-F, 4-Br B1 174 Cl CH3 NH S 2-F, 4-Cl B1175 Cl CH3 NH S 2-F, 4-CH3 B1 176 Cl CH3 NH S 2, 3, 4-Cl3 B1 177 Cl CH3 NH S 4-CH3 B-2 ---------- ---------- [0023]
[Table 9]
** 1 Table (continuation) ---------- Compound No. R1 R2 X Y Wn B ---------- 178 Cl CH3 NH S 3 4-Cl2 B-2 179 Cl CH3 NH S 2-Cl-4-CH3 B-2 180 Cl CH3 NH S 3-Cl-4-CH3 B-2 181 ClCH3 NH S 2-F, 4-Cl B-2 182 ClCH3 NH S 2-F, 4-CH3 B-2 183 Cl CH3NH S 3-F, 4-CH3 B-2 184 Cl CH3 NHS 3-CH3, 4-CH3 B-2 185 Cl CH3 NH S2-F, 5-CH3 B-2 186 Cl CH3 NH S 3-Cl-4-F B-2 187 Cl CH3 NCHO S 4-CH3 B1 188 Cl CH3 NCHO S 3 4-Cl2 B1 189 Cl CH3 NCHO S 3-F, 4-CH3 B1 190 Cl CH3 NCHO S 2, 3, 4-Cl3 B1 191 Cl CH3 NCHO S 3-F, 4-CH3 B-2 192 Cl CH3 NH

S 2-Cl B19 193 Cl CH3 NH S4-Cl B19 194 Cl CH3NH SO 4-CH three B19 195 Cl CH3NH SO2 4-CF3 B19 196 Cl CH3NH S 4-OCH3 B19 197 Cl CH3 NH S 2 4-Cl2 B19 198 Cl CH3 NH S 2-Cl, 4-CH3 B19 199 Cl CH3 NH S 3-Cl, 4-CH3 B19 ---------- [0024]

[Table 10]

** 1 Table (continuation) ---------- Compound No. R1 R2 X Y Wn B ---------- 200 Cl CH3 NH S 2-F, 4-Cl B19 201 Cl CH3 NH S 2-F, 4-CH3 B19 202 Cl CH3 NH S 2, 3, 4-Cl3 B19 203 Cl CH3 NCHO S H B19 204 ClCH3 NCHO S 2-Cl B19205 Cl CH3NCHO S 4-Cl B19 206 Cl CH3 NCHO S 4-CH3 B19 207 Cl CH3NCHO S 4-CF3 B19 208 Cl CH3 NCHO S 4-OCH3 B19 209 Cl CH3 NCHO S 2 4-Cl2 B19 210 Cl CH3 NCHOS 2-Cl, 4-CH3 B19 211 Cl CH3 NCHO S 3-Cl, 4-CH3 B19212 Cl CH3 NCHO S 2-F, 4-Cl B19 213 Cl CH3 NCHO S 2-F, 4-CH3 B19 214 ClCH3 NCHO S 2, 3, 4-Cl3 B19 215 Cl CH3 NH S H B20 216 Cl CH3 NH S 2-Cl B20 217 Cl CH3 NH S 4-Cl B20 218 Cl CH3 NH S 4-CH3 B20 219 Cl CH3 NH S 4-CF3 B20 220 Cl CH3 NH S 4-OCH3 B20 221 Cl CH3 NH S2, 4-Cl2 B20 ---------- [0025]

[Table 11]

** 1 Table (continuation) ---------- Compound No. R1 R2 X Y Wn B ---------- 222 Cl CH3 NH S 2-Cl, 4-CH3 B20 223 Cl CH3 NH S 3-Cl, 4-CH3 B20 224 Cl CH3 NH S 2-F, 4-Cl B20 225 Cl CH3 NH S 2-F, 4-CH3 B20 226 Cl CH3 NH S 2, 3, 4-Cl three B20 227 Cl CH3 NCHO S H B20 228 Cl CH3NCHO S 2-Cl B20 229 Cl CH3 NCHO S4-Cl B20 230 Cl CH3 NCHO S 4-CH three B20 231 Cl CH3 NCHO S 4-CF3 B20 232 Cl CH3 NCHO S 4-OCH three B20 233 ClCH3 NCHO S 2 4-Cl2 B20 234 Cl CH3 NCHO S 2-Cl, 4-CH3 B20 235 Cl CH3 NCHO S 3-Cl, 4-CH3 B20 236 Cl CH3NCHO S 2-F, 4-Cl B20 237 Cl CH3 NCHO S 2-F, 4-CH3 B20 238 Cl CH3 NCHO S 2, 3, 4-Cl3 B20 239 Br CH3 NH S H B19 240 Br CH3 NH S 2-Cl B19 241 Br CH3 NH S 2 4-Cl2 B19 242 Br CH3 NH S 3-Cl, 4-CH3 B19 243 Br CH3 NH S 3-F, 4-CH3 B19 ---------- [0026]

[Table 12]

** 1 Table (continuation) ---------- Compound No. R1 R2 X Y Wn B ---------- 244 Br CH3 NH S 2, 3, 4-Cl3 B19 245 Br CH3 NCHO S 4-Cl B19 246 Br CH3 NCHO S 2 4-Cl2 B19 247 Br CH3 NH S 2 4-Cl2 B20 248 Br CH3 NH S 3-Cl, 4-CH3 B20 249Br CH3 NH S 3-Cl, 4-CH3 B21 250 Br CH3NH S 3-F, 4-CH three B21 251Br CH3 NH S4-Cl B22 252 Br CH3 NH S 2 4-Cl2 B22 253 Br CH3 NH S 2 4-Cl two B23 254 Br CH3 NH S 3-F, 4-CH3 B23 255 Br CH3 NH S 2 4-Cl2 B24 256 Br CH3 NH S 3-Cl, 4-CH3 B24 257 Br CH3 NH S 3-F, 4-CH3 B25 258 Br CH3 NH S 2, 3, 4-Cl3 B25 259 Br CH3 NH S 2 4-Cl2 B26 260 F CH3 NH S 2, 4-Cl2B19 261 F CH3NH S 3-Cl, 4-CH3 B20 262 F CH3 NH S 3-Cl, 4-CH3 B21 263 CH3 CH3 NH S 2 4-Cl2 B21264 CH3 CH3 NH S 3-Cl, 4-CH3 B21265 CH3 CH3 NH S 3-F, 4-CH3 B21 ---------- [0027]

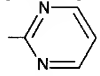
[Table 13]

** 1 Table (continuation) ---------- Compound No. R1 R2 X Y Wn B ---------- 266 CH3 CH3 NH S 2-F, 4-CH3 B21267 CH3 CH3 NH S 2-Cl, 4-CH3 B21268 Cl CH3 NH S 2 4-Cl two B21269 Cl CH3 NH S 3-Cl, 4-CH three B21270 CH3 CH3 NH S4-Cl B22271 CH3 CH3 NH S 2 and 4-Cl2 B22272 CH3 CH3 NH S 3-Cl, 4-CH3 B22273Cl CH3 NH S 2 4-Cl2 B22274 Cl CH3 NH S 3-Cl, 4-CH3

B22275 CH3 CH3 NH S 2 4-Cl2 B23276 CH3 CH3 NH S 3-Cl, 4-CH3 B23277 CH3 CH3 NH S 2-F, 4-Cl B23278 CH3 CH3 NH S 3-F, 4-CH3 B23279 Cl CH3 NH S 3-Cl, 4-CH3 B23280 CH3 CH3 NH S 2 4-Cl2 B24281 CH3 CH3 NH S 3-Cl, 4-CH3 B24282 Cl CH3 NH S 2 4-Cl2 B24283 Cl CH3 NH S 3-Cl, 4-CH3 B24284CH3 CH3 NH S 2, 4-Cl2B25285 Cl CH3 NH S 3-Cl, 4-CH3 B25286 CH3 CH3 NH S B1-B26 express the following chemical structures all over the 2 and 4-Cl2 B26 ---------- ---------- above-mentioned table.

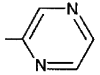
[0028]

[Formula 4]



B1 ,

B2 ,



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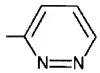
B4 ,



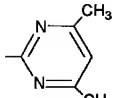
B5 ,

B6 .

[0029]

[Formula 5]


B7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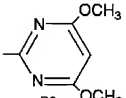
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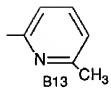
B10


B11


B12

[0030]
[Formula 6]



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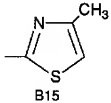
B14 ,



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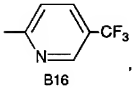

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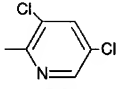

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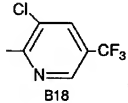

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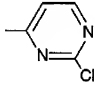

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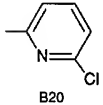
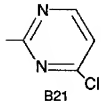


B20 ,

[0031]
[Formula 7]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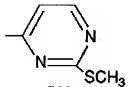
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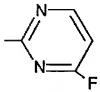
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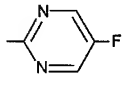
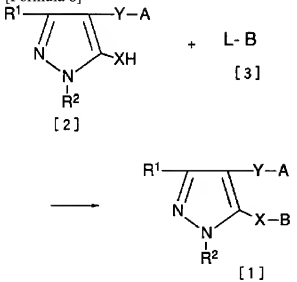

B26

[0032] Next, a reaction scheme shows the manufacturing method of this invention compound, and it explains below.

[0033] Reaction scheme (process 1)

[0034]

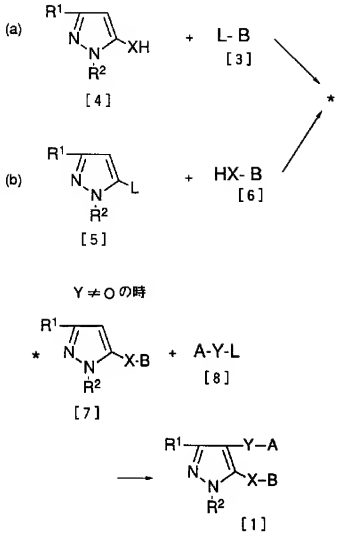
[Formula 8]



[0035] (Process 2)

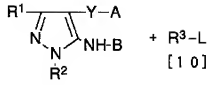
[0036]

[Formula 9]

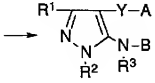


[0037] (Process 3)
[0038]
[Formula 10]

X=N-R³, R³ ≠ H の時

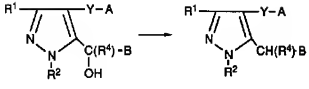


[9] [10]



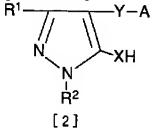
[11]

[0039] (Process 4)
[0040]
[Formula 11]
X=CH(R⁴)の時



[12] [13]

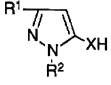
[0041] (Process 1)
Formula [2]: [0042]
[Formula 12]



[2]

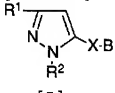
[0043] R1, R2, Y, and A express the same semantics as the above among [type, and X expresses -N(R3)-.] The permutation pyrazole come out of and shown, and formula [3]:L-B [3]
L expresses leaving groups, such as a halogen atom, among [type, and B expresses the same semantics as the above.] this invention compound can be manufactured by coming

out and making the heterocycle shown react. in this case, X of a formula [2] -NCOR4 or -NSO two R5 it is -- the time -- after treatment etc. -- setting -- hydrolysis -- receiving -- X of a product It may be obtained by -NH.
[0044] In the above-mentioned reaction, although a solvent is not necessarily required, as a solvent used, polar solvents, such as nitril, such as ester, such as ether, such as halogenated hydrocarbon, such as hydrocarbons, such as toluene, a xylene, and chlorobenzene, and a dichloroethane, diisopropyl ether, and dioxane, and ethyl acetate, and an acetonitrile, dimethyl sulfoxide, and dimethylformamide, are mentioned, for example. Moreover, organic bases (a pyridine, triethylamine, etc.) and inorganic bases (potassium carbonate, sodium hydride, etc.) may be added if needed.
[0045] Moreover, copper salt and a copper complex may be added as a catalyst if needed. The range of the heterocycle shown by the formula [3] to 1Eq of permutation pyrazoles the amount of the agent used for the above-mentioned reaction is indicated to be by the formula [2] is 1-5Eq. Although reaction temperature is obtained for arbitration in the above-mentioned reaction, room temperature -200 degree C or the reflux temperature of a solvent is usually desirable. After reaction termination can obtain the specified substance by performing the usual after treatment.
[0046] (Process 2)
(a) Formula [4]: [0047]
[Formula 13]



[4]

[0048] R1 and R2 express the same semantics as the above among [type, and X expresses -N(R3)-.] It is formula [7]: [0049] by making the heterocycle which comes out and is shown by the pyrazole shown and the formula [3] react using a suitable solvent and a suitable base if needed.
[Formula 14]



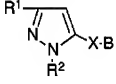
[7]

[0050] R1, R2, X, and B express the same semantics as the above among [type.] It manufactures. in this case, X of a formula [4] -NCOR4 or -NSO two R5 it is -- the time -- after treatment etc. -- setting -- hydrolysis -- receiving -- X of a formula [7] It may be obtained by -NH. In the above-mentioned reaction, polar solvents, such as nitril, such as ester, such as ether, such as halogenated hydrocarbon, such as hydrocarbons, such as toluene, a xylene, and chlorobenzene, and a dichloroethane, diisopropyl ether, and dioxane, and ethyl acetate, and an acetonitrile, dimethyl sulfoxide, and dimethylformamide, are mentioned as a solvent used, for example.

[0051] Moreover, as a base used, potassium carbonate, sodium hydride, etc. are mentioned, for example. Moreover, copper salt, a copper complex, etc. may be added as a catalyst if needed. Although reaction temperature is obtained for arbitration in the above-mentioned reaction, room temperature -200 degree C or the reflux temperature of a solvent is usually desirable.
[0052] (b) Formula [5]: [0053]
[Formula 15]

[5]

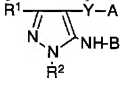
[0054] R1 and R2 express the same semantics as the above among [type, and L expresses leaving groups, such as a halogen atom.] The pyrazole come out of and shown, and formula [6]:HX-B [6]
B expresses the same semantics as the above among [type, and X expresses -N(R3)-.] It is formula [7]: [0055] by coming out and making the heterocycle shown react using a suitable solvent and a suitable base if needed.
[Formula 16]



[7]

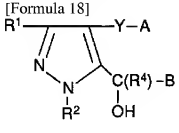
[0056] R1, R2, X, and B express the same semantics as the above among [type.] It manufactures. in this case, X of a formula [6] -NCOR4 or -NSO two R5 it is -- the time -- after treatment etc. -- setting -- hydrolysis -- receiving -- X of a formula [7] -NH It may be obtained. In the above-mentioned reaction, polar solvents, such as nitril, such as ester and an acetonitrile, dimethyl sulfoxide, and dimethylformamide, are mentioned to ether, such as halogenated hydrocarbon, such as hydrocarbons, such as toluene, a xylene, and chlorobenzene, and a dichloroethane, diisopropyl ether, and dioxane, ethyl acetate, etc. as a solvent used, for example.
[0057] Moreover, potassium carbonate, sodium hydride, etc. are mentioned as a base used. Moreover, copper salt, a copper complex, etc. may be added as a catalyst if needed. Although reaction temperature is obtained for arbitration in the above-mentioned reaction, room temperature -200 degree C or the reflux temperature of a solvent is usually desirable.
[0058] The next above (a) Or (b) The pyrazole shown by the obtained formula [7], and formula [8]:A-Y-L [8]
As for the inside A of [type, the same semantics as the above is expressed, Y expresses the same semantics as the above except an oxygen atom, and L expresses leaving groups, such as a halogen atom.] this invention compound can be manufactured by coming out and making the compound shown react using a suitable solvent and a suitable base if

needed.
[0059] In the above-mentioned reaction, polar solvents, such as nitril, such as ester, such as ether, such as halogenated hydrocarbon, such as hydrocarbons, such as toluene, a xylene, and chlorobenzene, a dichloroethane, chloroform, and a carbon tetrachloride, diisopropyl ether, and dioxane, and ethyl acetate, and an acetonitrile, dimethyl sulfoxide, and dimethylformamide, are mentioned as a solvent used, for example.
[0060] Moreover, a pyridine, triethylamine, potassium carbonate, etc. are mentioned as a base used. Although reaction temperature is obtained for arbitration in the above-mentioned reaction, 0 degree C - 100 degrees C are usually desirable.
(Process 3) It is formula [9]: [0061] at the time of X=N-R3 and R3 !=H.
[Formula 17]



[9]

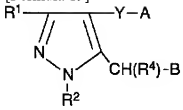
[0062] R1, R2, Y, A, and B express the same semantics as the above among [type.] Pyrazole come out of and shown, and formula [10]:R3-L [10]
Among [type, R3 </SUP> expresses the same semantics as the above except a hydrogen atom, and L expresses leaving groups, such as a halogen atom.] this invention compound can be manufactured by coming out and making the compound shown react using a suitable solvent and a suitable base if needed.
[0063] In the above-mentioned reaction, polar solvents, such as nitril, such as ester, such as ether, such as halogen hydrocarbons, such as hydrocarbons, such as benzene, toluene, and a xylene, a dichloroethane, chloroform, and a carbon tetrachloride, diisopropyl ether, a tetrahydrofuran, and dioxane, and ethyl acetate, and an acetonitrile, dimethyl sulfoxide, and dimethylformamide, are mentioned as a solvent used, for example.
[0064] Moreover, as a base used, inorganic bases, such as organic bases, such as a pyridine and triethylamine, and potassium carbonate, sodium hydride, are mentioned. In the above-mentioned reaction, although reaction temperature is obtained for arbitration, 0 degree C - 100 degrees C are usually desirable.
[0065] (Process 4) It is formula [12]: [0066] at the time of X=CH (R4).
[Formula 18]



[12]

[0067] R1, R2, Y, A, B, and R4 express the same semantics as the above among [type.] By coming out and making the compound shown react using a suitable reducing agent, it is formula [13]: [0068].

[Formula 19]



[13]

[0069] R1, R2, Y, A, B, and R4 express the same semantics as the above among [type.] It can come out and this invention compound shown can be manufactured. as the reducing agent used in the above-mentioned reaction -- P2 I4 etc. -- the Lynn system compound is mentioned.

[Translation done.]